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Claes

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[54] CONTINUOUS FLOW MIXING APPARATUS

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[73] Assignee: **Agfa-Gevaert**, Mortsel, Belgium

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[30] **Foreign Application Priority Data**

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Mar. 4, 1970	Great Britain	15948/70

[52] **U.S. Cl.** .... **259/7**, 23/252 R
[51] **Int. Cl.** **B01f 7/08**
[58] **Field of Search** 259/7, 8, 23, 24, 43, 44; 23/252

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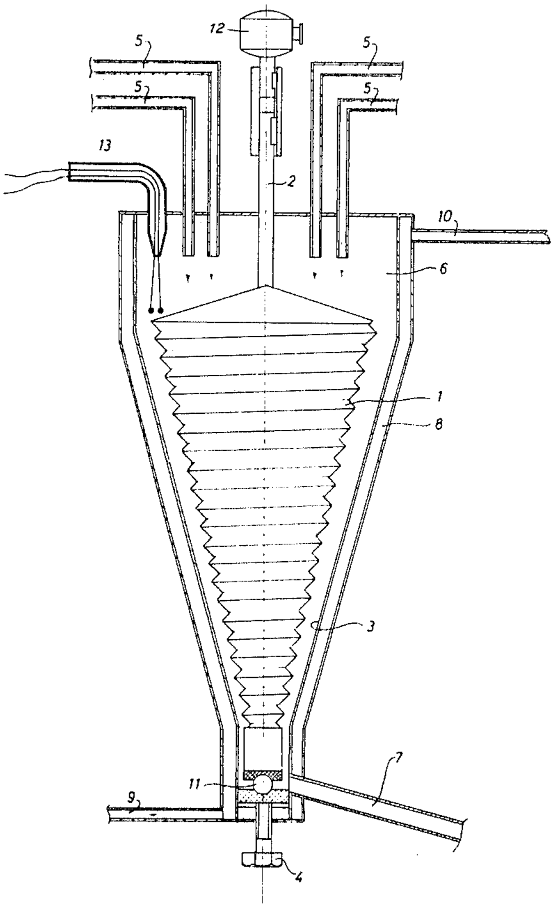
Primary Examiner—Robert W. Jenkins
Attorney, Agent, or Firm—William J. Daniel

[57] ABSTRACT

A continuous flow liquid mixing apparatus in which a rotor is arranged coaxially within a housing with the mutually facing peripheral surfaces thereof defining a clearance space in the form of an annular passage with a gradually and continuously decreasing radial cross-section. This annular passage serves as a mixing zone having an inlet opening at the larger section end and an outlet opening at the smaller section end thereof. The mutually facing peripheral walls of the rotor and housing are continuous and smooth and free of any interruptions or perforations and preferably the radial dimension of the clearance space is not more than 10 mm and optimally not more than 5 mm. Drive means are provided for imparting relative rotation to the rotor or housing to apply shearing forces to liquid passing through the mixing zone. In the region upstream of the mixing zone, the mutually facing peripheral wall sections of the rotor and housing diverge sharply to provide a feeding space which is free of interruptions in the form of baffles, grooves or the like and the liquid or liquids to be mixed are introduced into this feeding space.

16 Claims, 19 Drawing Figures



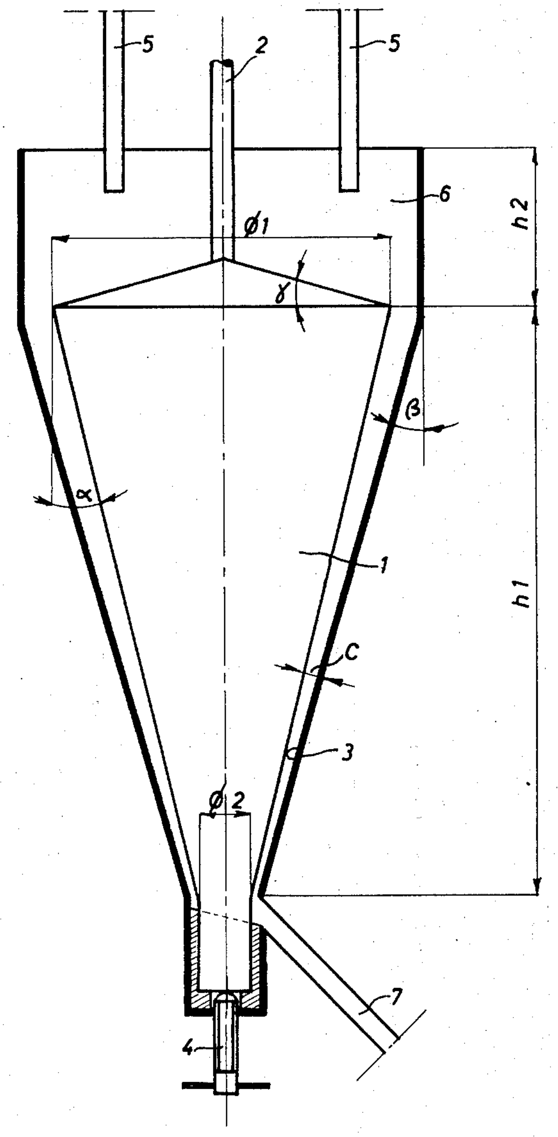


Fig. 1

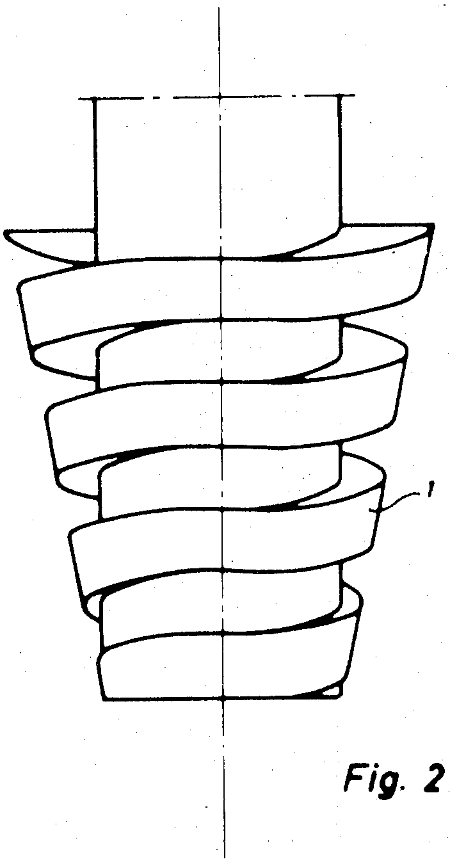
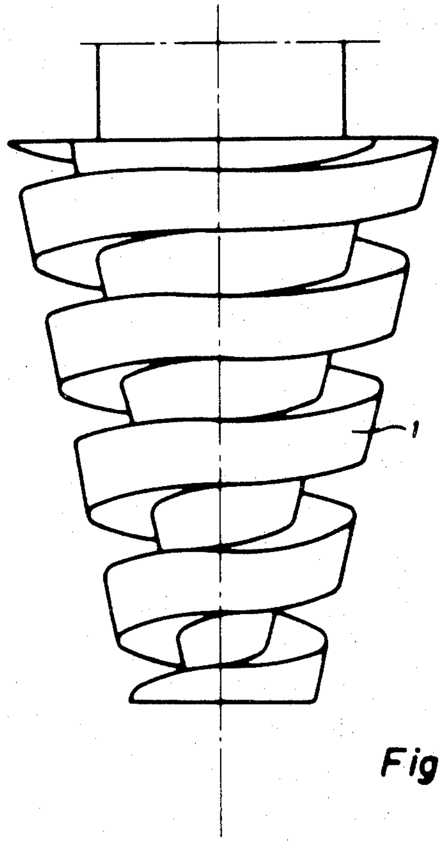


Fig. 2



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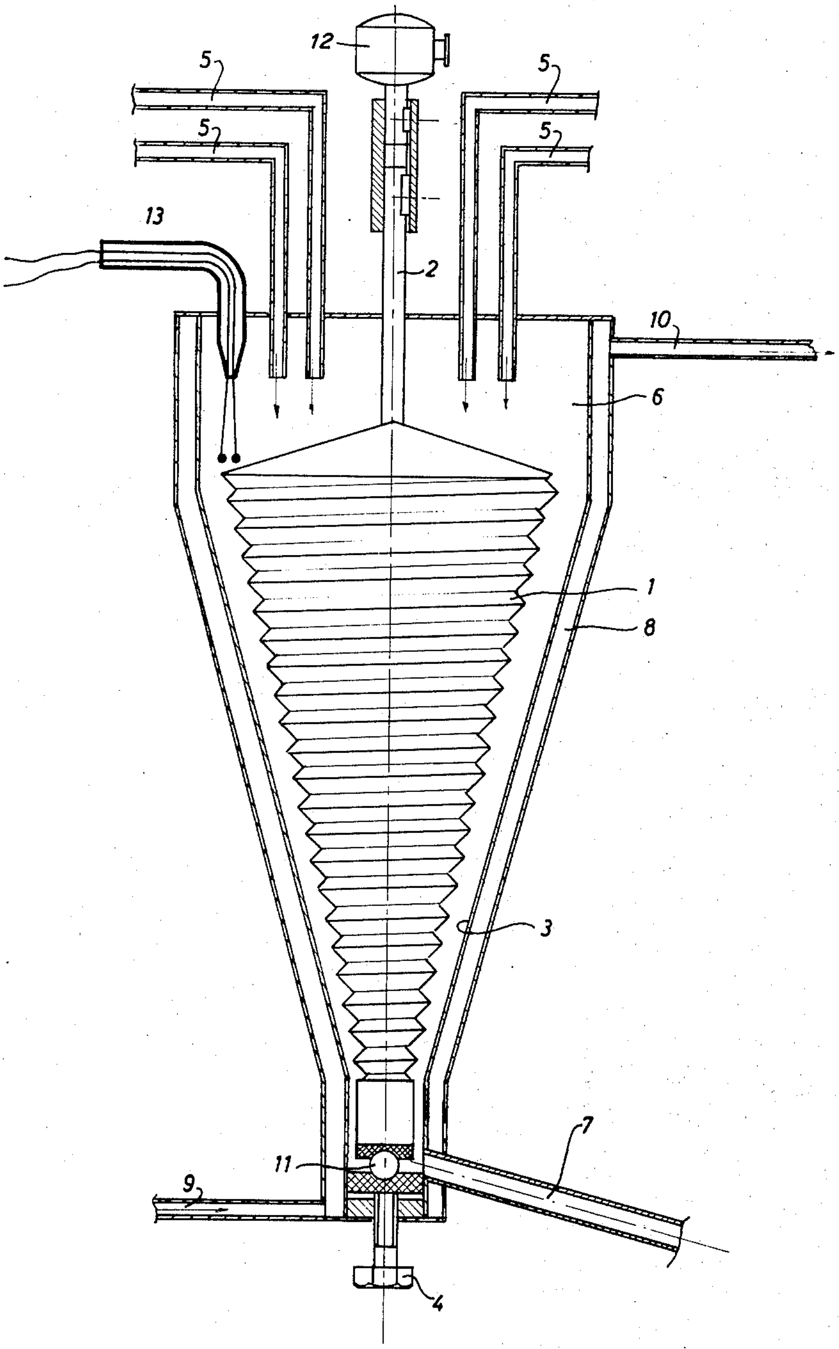

Fig. 4

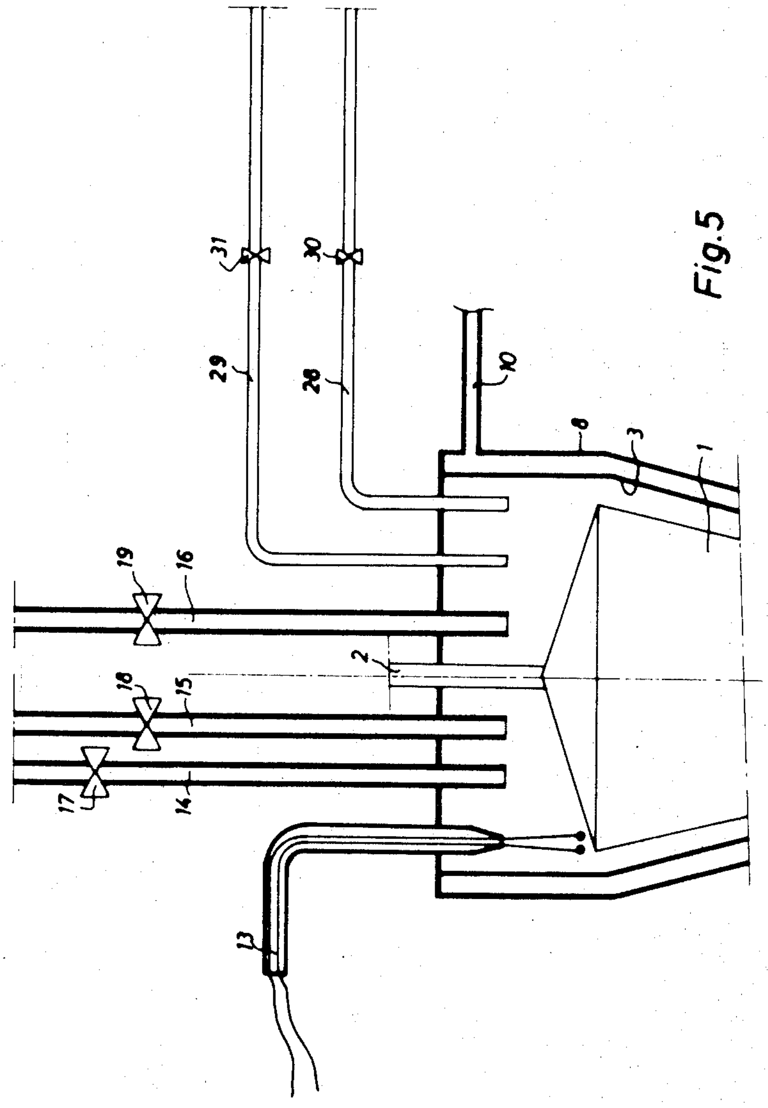

Fig.5

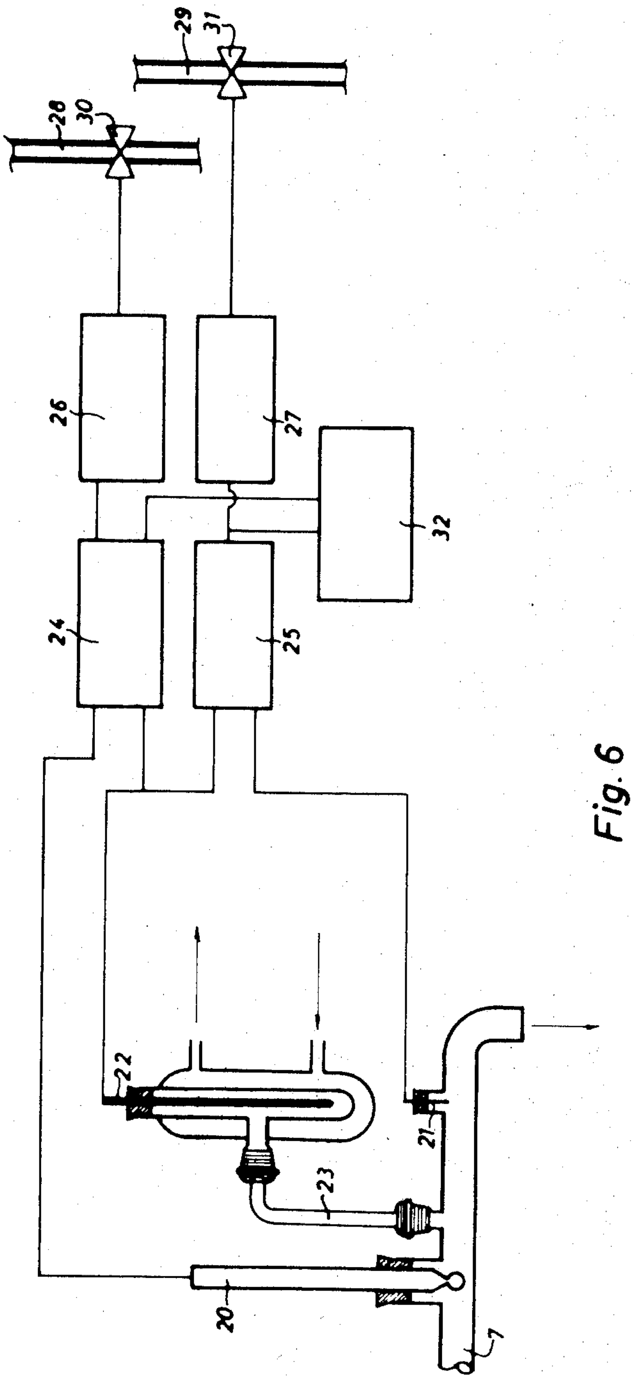

Fig. 6

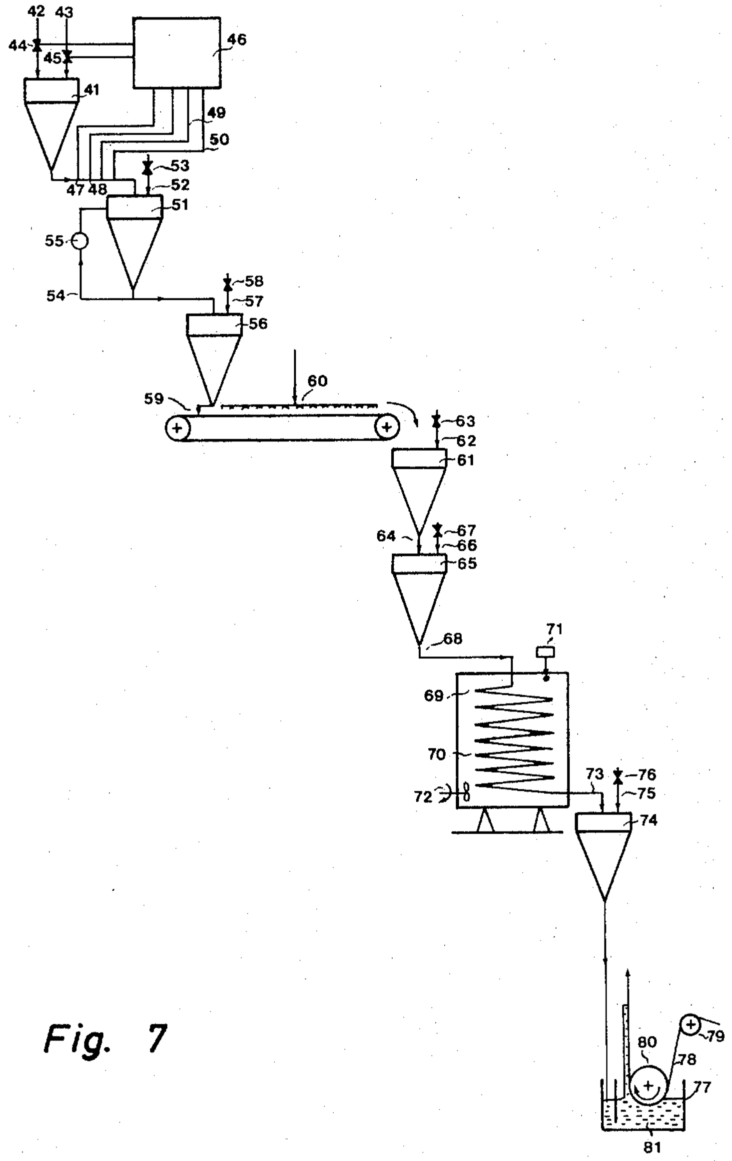
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Fig. 7

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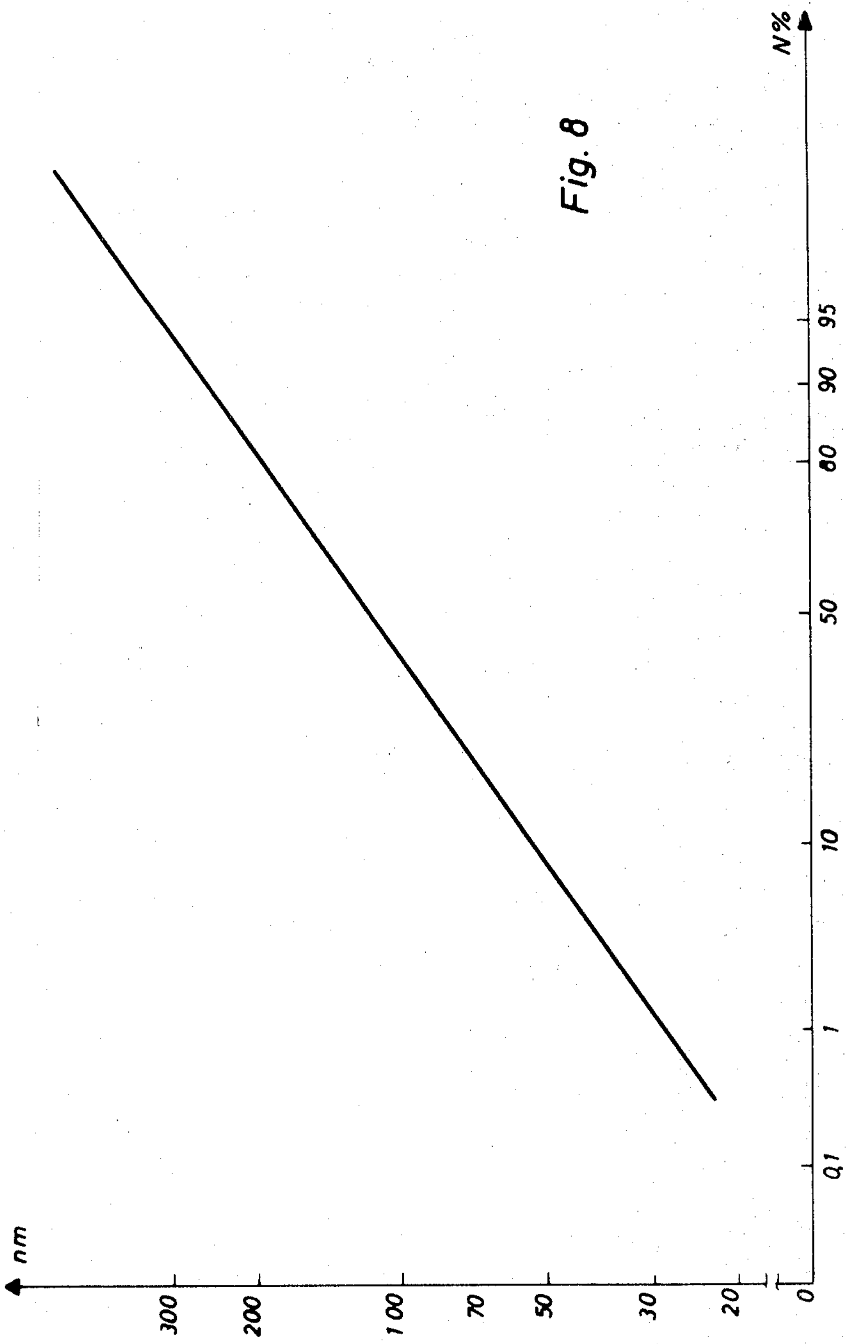


Fig. 8

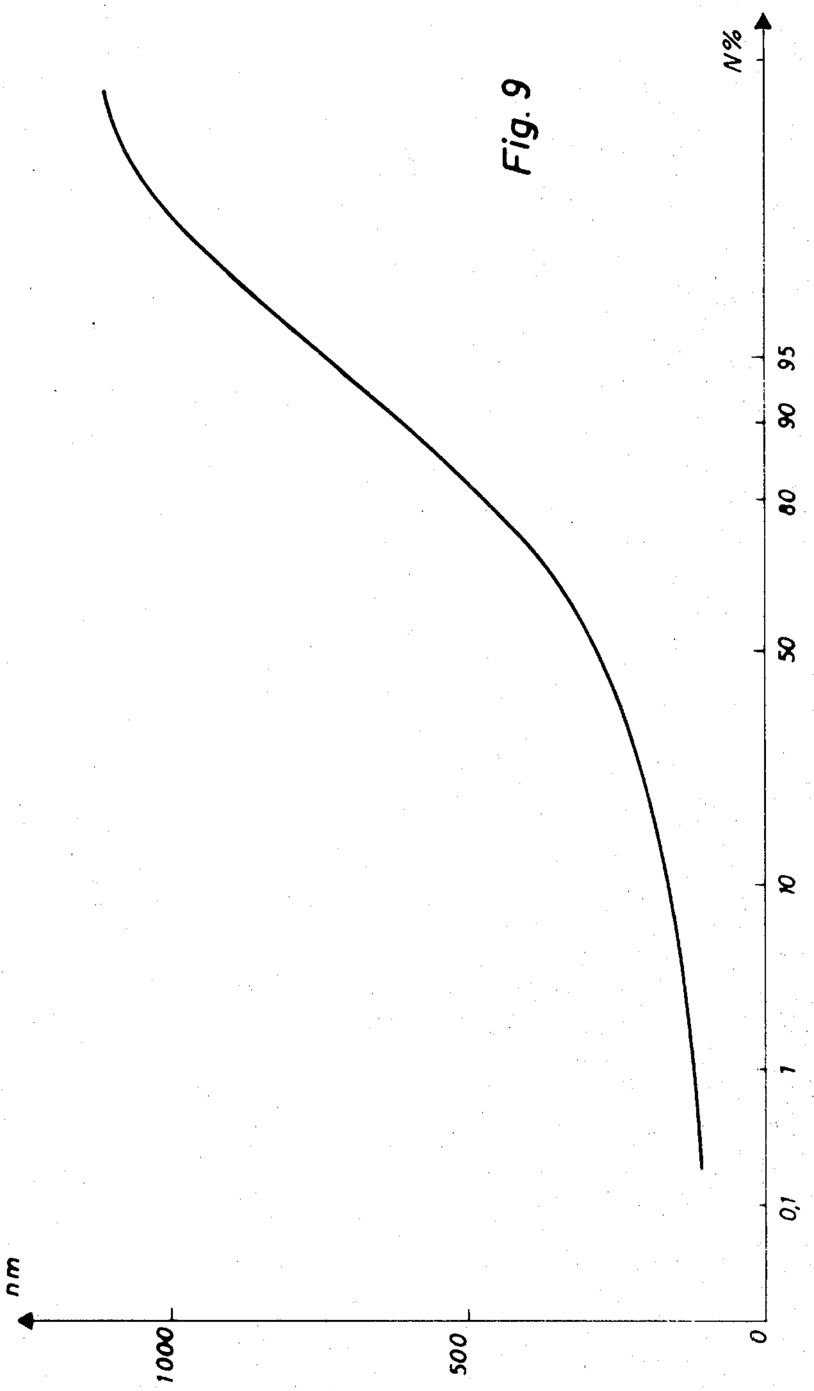


Fig. 9

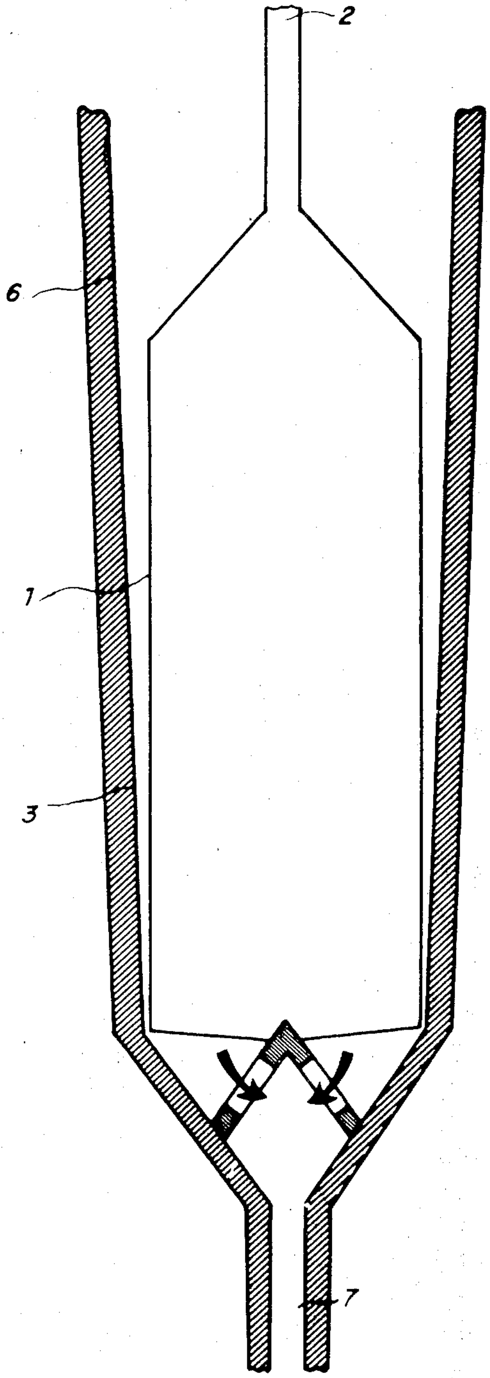


FIG. 10

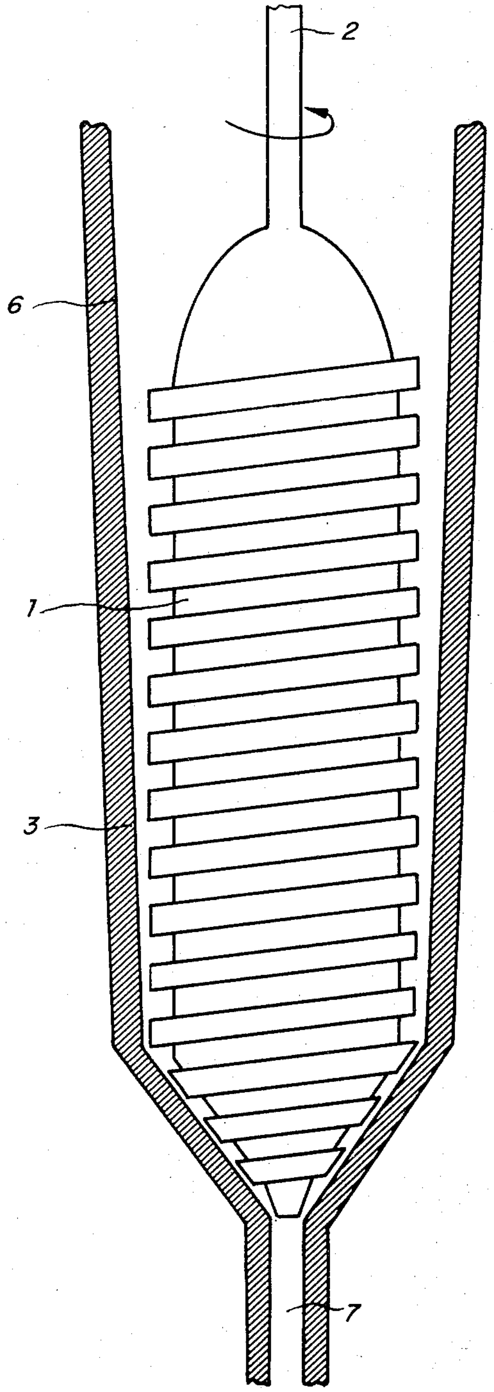


FIG. 11

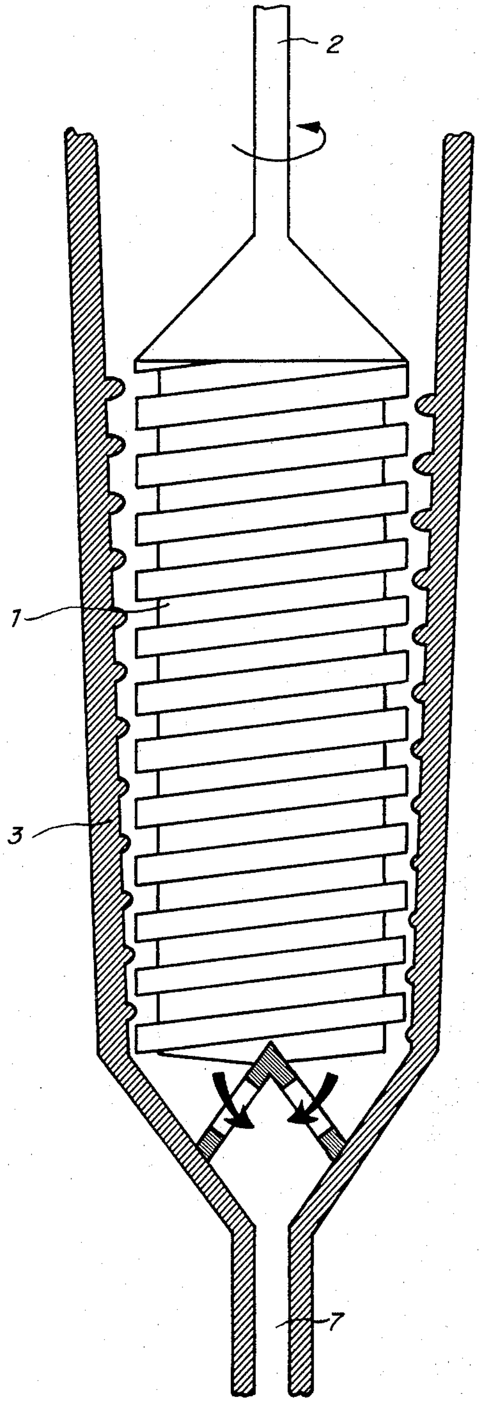


FIG. 12

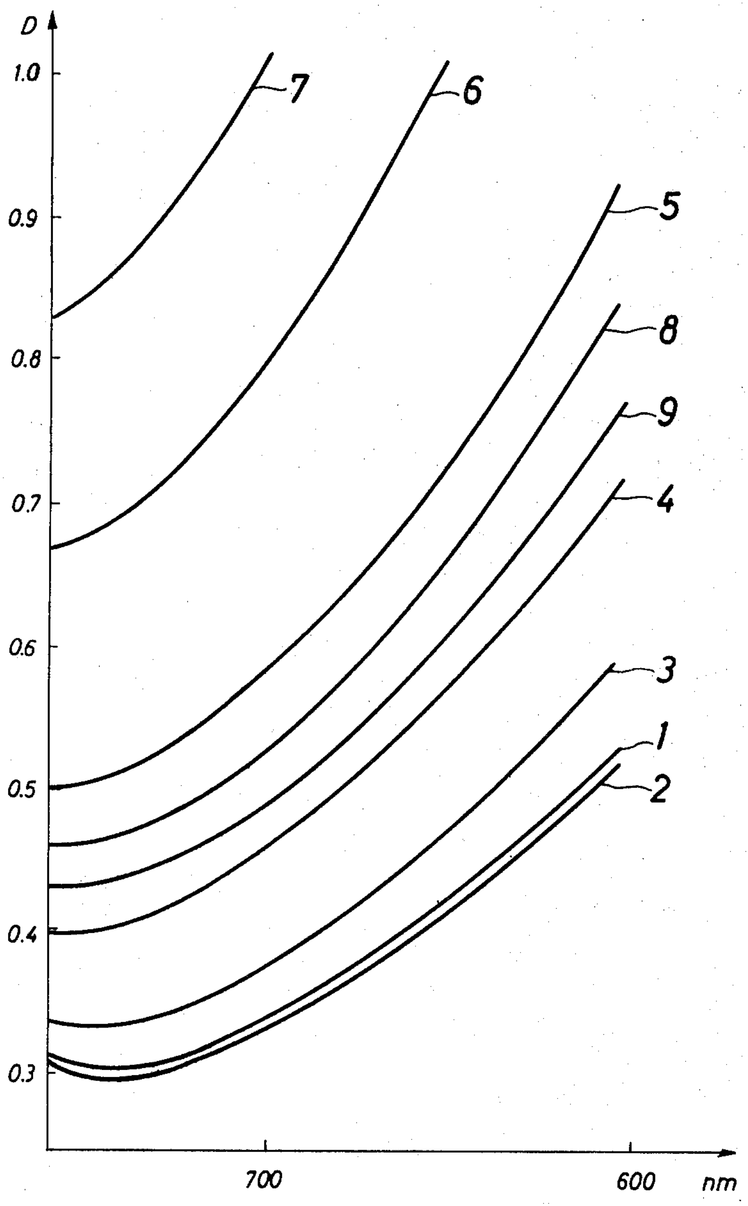


Fig. 13

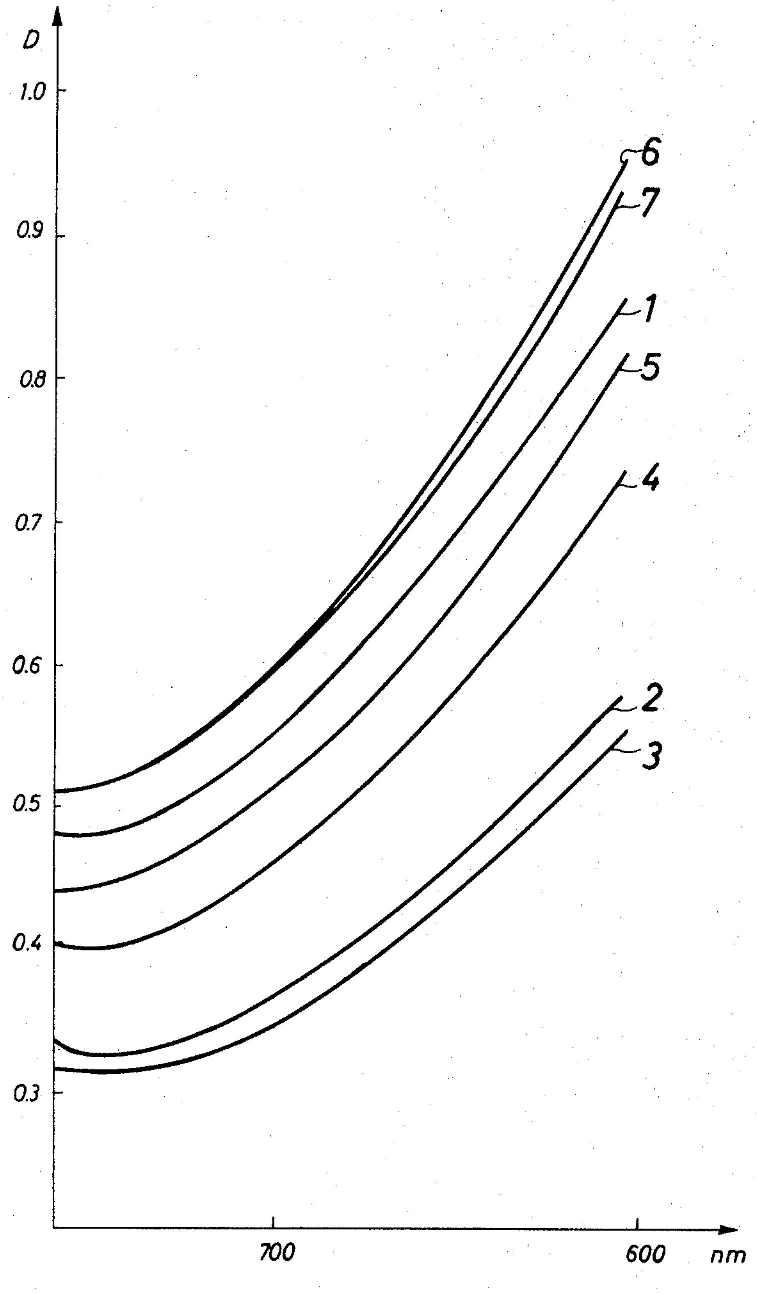


Fig. 14

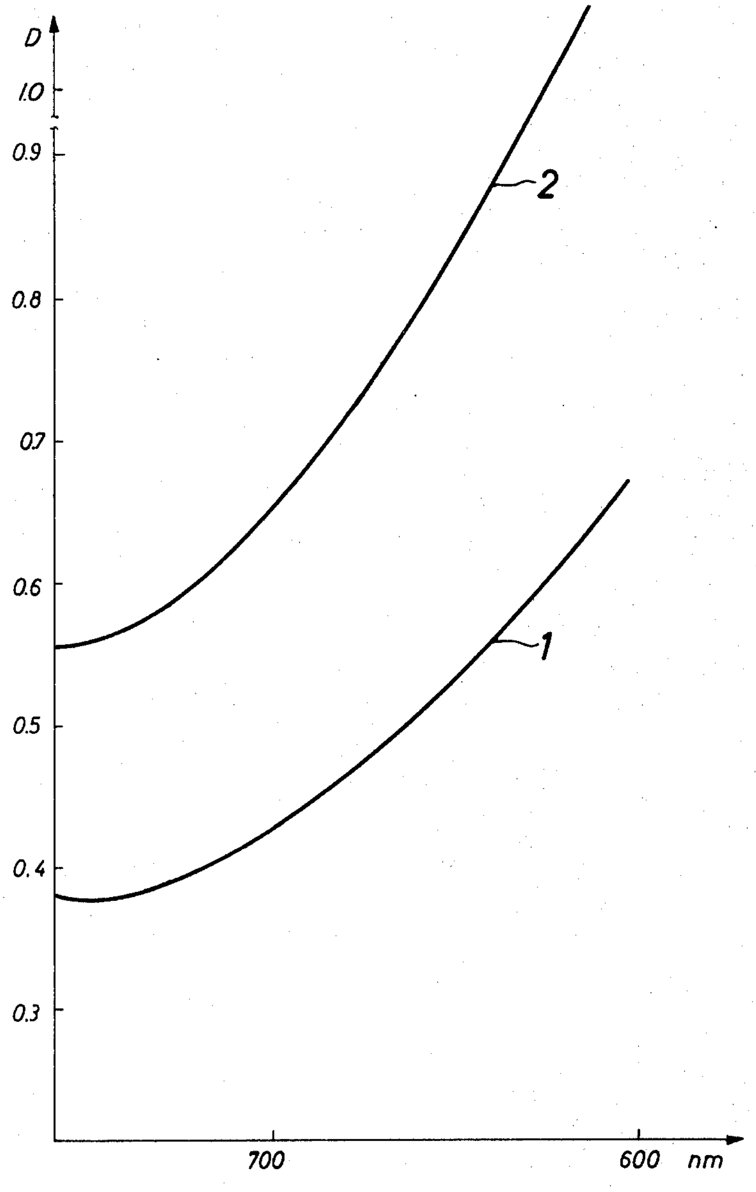


Fig. 15

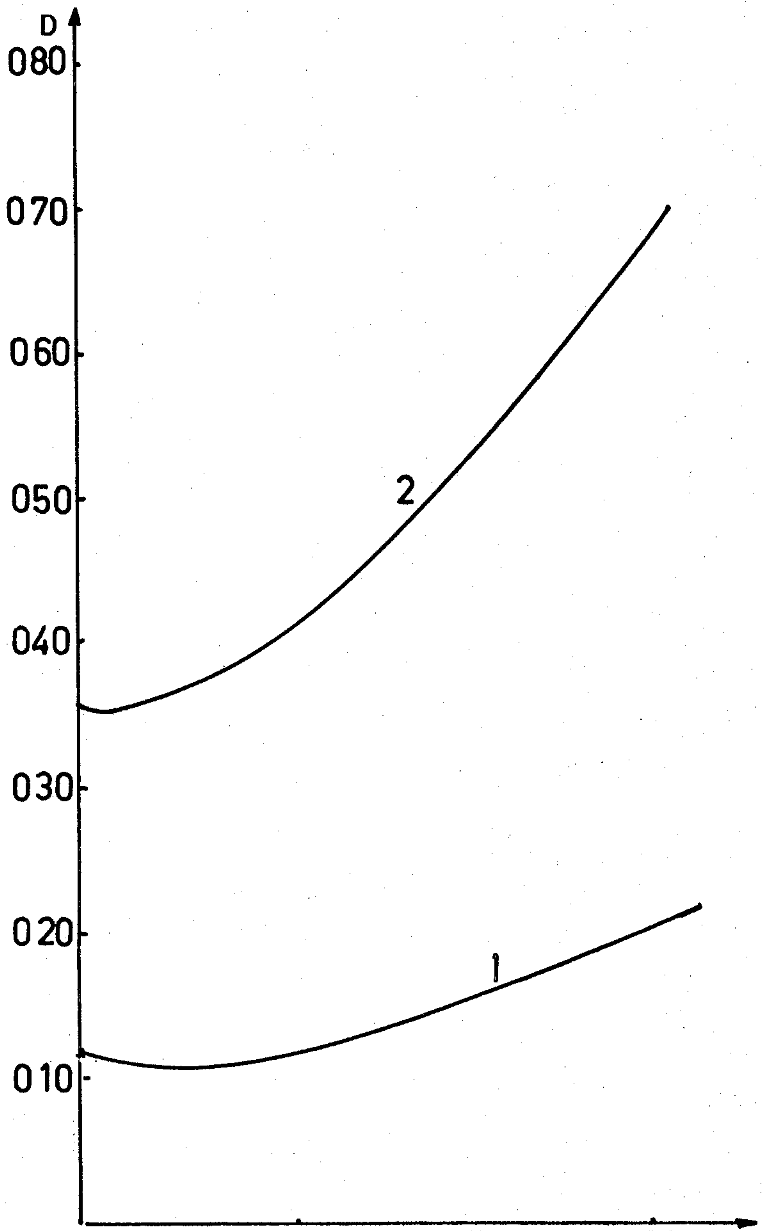


Fig 16

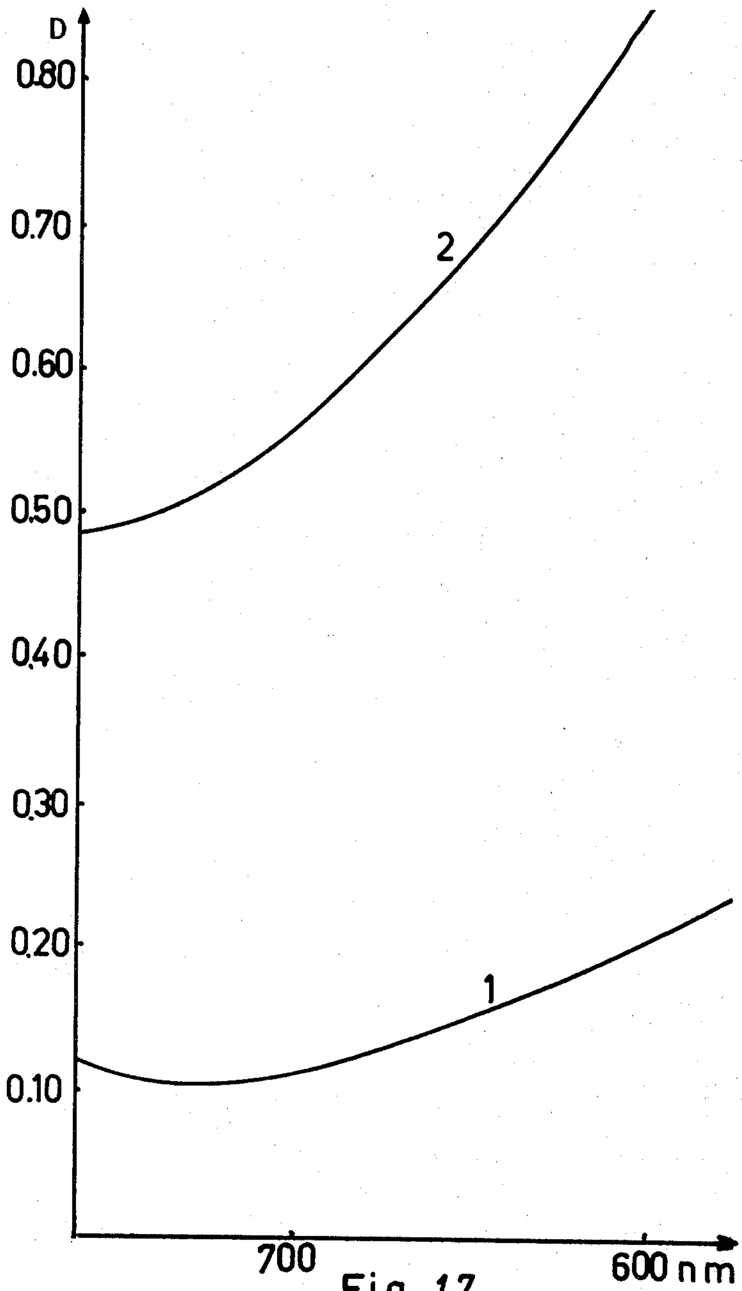


Fig 17

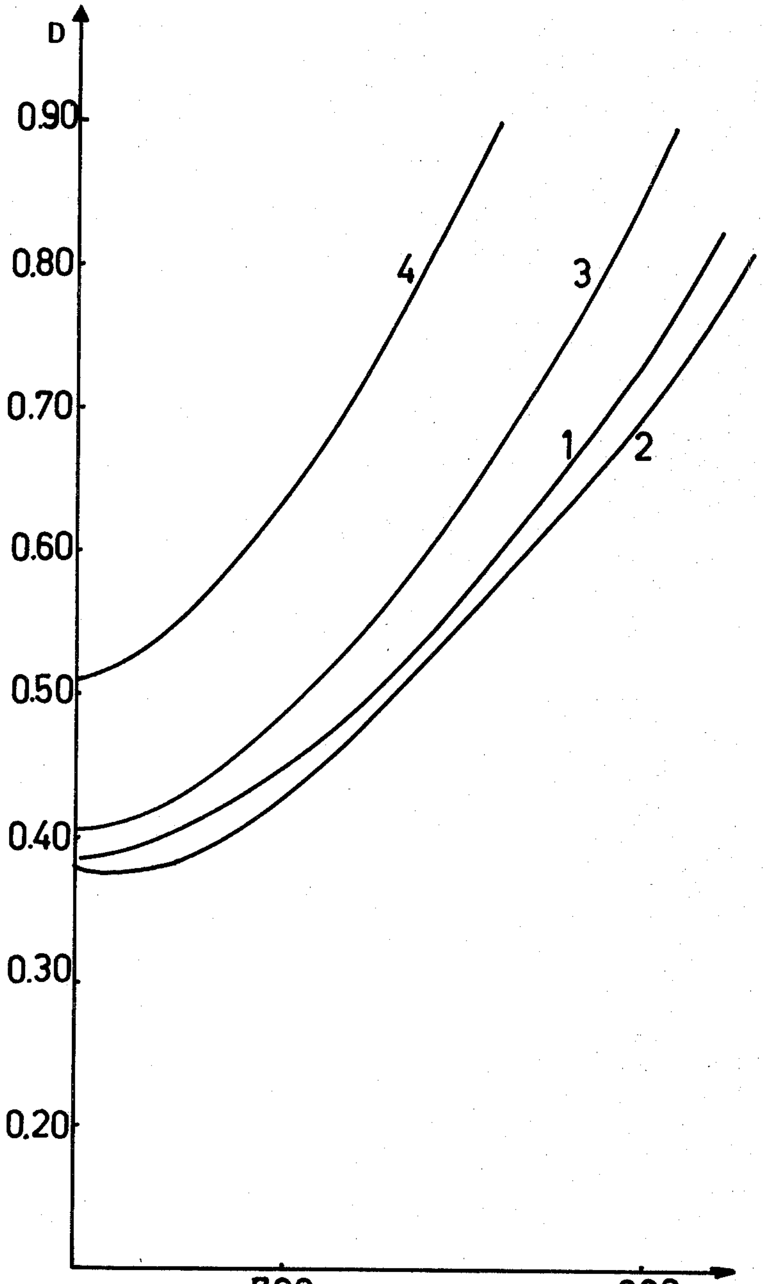


Fig 18

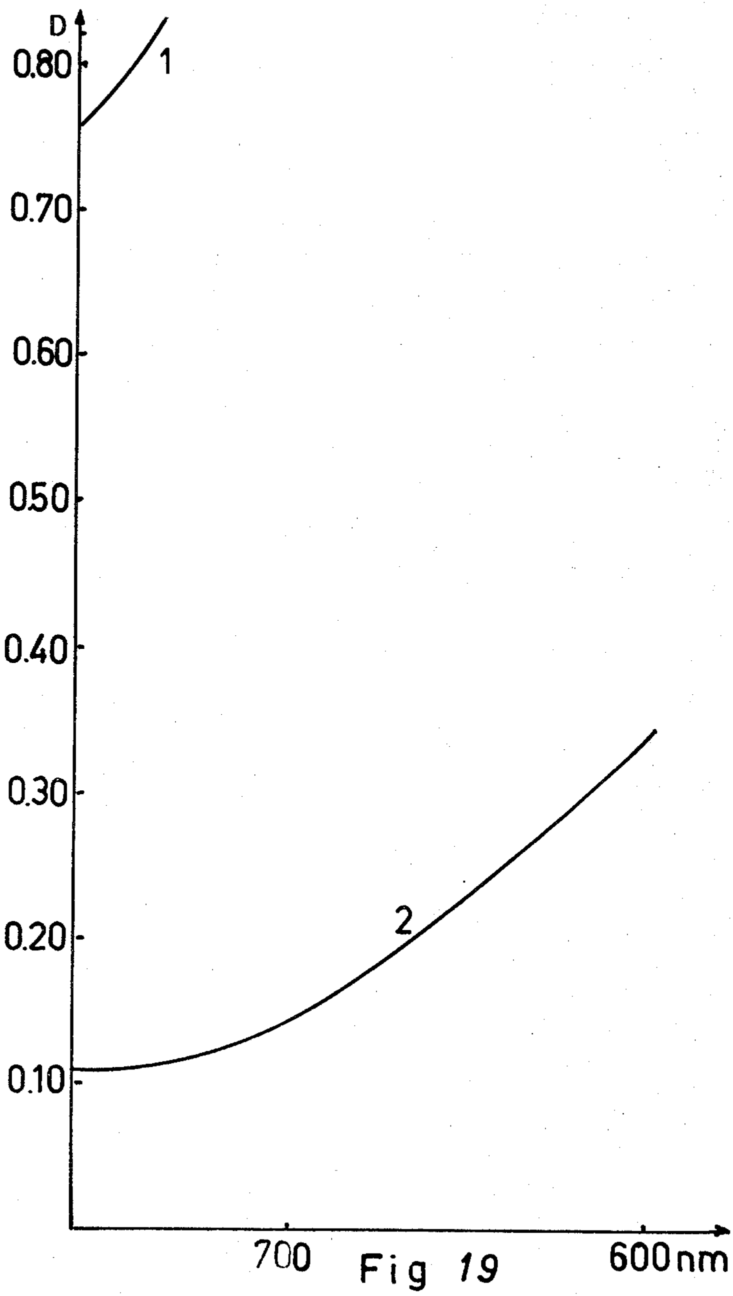


Fig 19

CONTINUOUS FLOW MIXING APPARATUS

The invention has been made in the course of research concerned with the preparation of fine grained silver halide emulsions. In that research it was found that emulsions of extremely fine grain size can be formed by bringing the reactants together in very small quantities at a time and generating shear forces throughout the volume of the mixture during the precipitation. The present invention provides apparatus by means of which this principle can be applied in a rapid and continuous mixing process.

Apparatus according to the present invention comprises inner and outer bodies defining between them an annular passage through which components can flow continuously from one end to the other of said passage, said bodies being relatively rotatable for subjecting the components in said passage to tangential frictional forces and having facing profiles such that said frictional forces can induce shearing stresses creating turbulence throughout the whole volume of the liquid passing through such passageway when the apparatus is in use.

In order that turbulence can be created through the whole volume of liquid in the annular passage, the clearance between the inner and outer bodies must be small. The maximum permissible clearance depends partly on the relative rotational speed of the bodies which is to be attained. In general, it is preferable for the clearance to be not more than 10 mm and most preferably not more than 5 mm at any position in the passage.

Only small liquid volumes are brought together at any moment in the annular passage and precipitate-forming reactions such as that involved in silver halide emulsion preparation can be performed so that the quantities of the reactants entering the annular passage at any given moment are used up substantially entirely in nucleation and not to any substantial extent in producing grain growth.

It has now been found that the continuous preparation of silver halide grains by mixing aqueous liquids separately containing silver ions and halide ions proceeds advantageously in a continuous flow mixing apparatus which comprises a central inner body (rotor) and an outer body (casing or housing) surrounding the mantle surface of the rotor, and wherein the housing and rotor are arranged co-axially and form a clearance or layer space in the form of an annular passage having a section continuously decreasing in a direction perpendicular to the axis of revolution, said layer space serving at its larger section as the inlet for the mixing zone that is formed between the mantle of the rotor and the surrounding surface of the housing, and serving at its smaller section as the outlet for the mixing zone and wherein the facing walls defining the layer space are non-perforated, smooth or helicoidally grooved or have a roughness and/or dot-like protuberances that contribute(s) to create turbulence in a liquid that is forced to pass through said clearance, the rotor and/or housing being provided with an actuating means for its or their rotational movement along said axis and wherein said housing departing from the zone of larger sections and extends non-perpendicularly, preferably aligns with the axis of revolution, above the rotor and wherein the top surface of the rotor in the zone of the longer sections has a surface free from guiding slots that could isolate separate portions of liquid.

The apparatus of the present invention can be used in a method of mixing a plurality of liquids that contain ingredient(s) which form by mixing a disperse or discontinuous phase, characterized in that the liquids to be mixed are continuously introduced into a passage-way over the whole transverse cross-section of which the infed liquids are maintained in continuous flow away from the feed point(s) and within which the liquid mass flowing through said passage-way is subjected to forces creating turbulence throughout substantially its entire volume.

As ingredients are used, e.g., those that by chemical reaction form a solid disperse phase such as crystalline grains. In that respect are particularly mentioned silver halide grains produced from a dissolved silver salt and a dissolved halide applied from separate aqueous liquids.

In such a method the different liquids that contain ingredients for a chemical reaction forming a precipitate are continuously and separately fed in the mixing passage-way, the transverse cross-sectional dimensions of the mixing passage-way and the degree of turbulence being such that the quantities of reactants entering the passage-way at any moment are used up substantially entirely in nucleation and not to any substantial extent in producing grain growth.

Said passage-way has preferably transverse cross-sectional dimensions, which allow the flow-through of a liquid film having a thickness less than 5 mm. The liquid mass in said passage-way has preferably at every point an average velocity component in the direction in which the liquid advances along the passage-way and is subjected to shearing stresses throughout or substantially throughout its entire volume in the passage-way resulting in turbulent flow.

Turbulent flow can be obtained by exerting on the liquid mass in said passage-way in the flow direction a pressure sufficient to keep the Reynolds number well above the critical value at which turbulent flow conditions occur.

Turbulent flow conditions can likewise be obtained by moving a wall or walls of the passage-way at a sufficient velocity or velocities to create the turbulent flow by frictional forces produced by contact of the liquid mass with said moving wall or walls.

Such is the case in the apparatus according to the present invention wherein the passage-way is an annular layer space defined by walls that are continuously relatively rotated about an axis for generating frictional forces, and wherein the quanta of liquids entering the passage-way at any time do not become mixed with material that already has been subjected to shearing forces in the passage-way.

In an apparatus according to the present invention, one or each of the facing surfaces of the inner and outer bodies may be formed with a helical groove but in order that liquid in the groove or grooves shall not be shielded from the tangential shearing forces the inclination of the or each groove to the axis of revolution should be in excess of 45° and the depth of the grooves preferably not larger than 5 mm. It is considered very desirable for the facing profiles of the bodies and the length of the annular passage to be such that each quantum of the liquid entering the passage by gravity can remain therein during multiple relative revolutions of said bodies.

Owing to the fact that the cross-sectional area of the annular passage decreases towards the discharge end, the axial velocity of introduced liquid increase in the direction of the discharge end and makes that the shear forces vary along the passage-way from the entry to the discharge end thereof.

The facing profiles of the relatively rotatable bodies are preferably conical.

In operating the apparatus best mixing results are obtained by taking care that the shearing stress schedule to which the mixture is exposed during its residence time in the annular passage is substantially the same for all quanta of the mixture. This means, inter alia, that all such quanta should remain in the passage for substantially the same length of time. Accordingly there should be a continuous flow away from the feed point or feed points at all positions in the annular passage with no possibility of random circulation of significant portions of the liquid between zones at different distances from such feed point(s).

While the invention has been made primarily for application in the preparation of silver halide emulsions, apparatus according to the invention can be used in the preparation of any dispersions, whether emulsions or suspensions, by mixing liquids constituted so that the mixing causes the formation of a disperse phase. For example, one liquid may contain a dissolved substance which precipitates on modification of the pH of the liquid and the other liquid may contain an ingredient which brings about such pH modification. As another example, one liquid may contain a dissolved substance and the other liquid may be a liquid that is miscible with the first liquid but is a non-solvent for such substance. Alternatively the different liquids may contain ingredients that react to form a precipitate as in the formation of silver halide grains by the reaction of a soluble silver salt and a soluble halide. Apparatus according to the invention can also be used for the purpose of reducing the size of the dispersed droplets of an emulsion, or continuous melting of thermoplastic material, e.g., the melting of silver halide emulsion noodles.

Particularly for carrying out precipitate-forming chemical reactions, the different liquids, the mixing of which causes the formation of the precipitate, should be continuously and separately fed into the annular mixing passage. Apparatus according to the invention accordingly preferably comprises at least two feed devices for separately feeding two liquids into the annular passage.

Preferably the mean diameter of the annular mixing passage in any plane normal to the axis of relative rotation of the inner and outer bodies is substantially less than the length of the annular passage measured from the feed to the discharge end thereof. The reason for this is that on the one hand it is necessary for the processes primarily in view to keep the annular passage filled with liquid and to do this while feeding only small quanta of liquid at a time into the passage, while on the other hand the passage has to be of sufficient length to ensure that the liquid material fed into it is subjected to the shearing forces for a sufficient length of time. Preferably the length of the passage is at least 1.25 times its mean diameter.

It is preferred to mount the inner body for rotation within the outer body, the latter being non-rotatable. The inner body may have an axially extending spindle by means of which it can be coupled to a motor.

The apparatus may be and preferably is arranged for use in a vertical orientation, e.g., with the axis of relative rotation of the inner and outer bodies substantially vertical, and for feed of the liquid material to the top of the annular passage under gravity.

According to a preferred design feature the top of the inner body, which is rotatable (rotor), has a top surface which slopes downwardly from a central region to its periphery. The liquid material can be released onto the top surface of the inner body so as continuously to flow into the top of the annular passage.

The provision of means for feeding liquid material into the annular passage under pressure is not excluded although preference is presently given to gravity feed.

It is important when preparing fine grain silver halide emulsions and when preparing various other dispersions with a narrow size range distribution of the disperse phase, to keep the Reynolds number above the critical value marking the transition from laminar to turbulent flow. It will be evident that the attainment of the critical Reynolds number can be realised in part by feeding the liquid material into the annular passage under positive and continuous pressure, in which case the speed at which the bodies have to be relatively rotated in order to establish the turbulent flow condition is not so great. However, in the embodiments at present preferred, the feed of liquid material is by gravity and the inner and outer bodies defining the annular mixing passage are relatively rotatable at sufficient speed to create the turbulent flow condition by virtue of the tangential frictional forces exerted on the liquid by the walls of the passage.

For convenience it will hereafter be assumed that the inner body alone is rotatable but it should be kept in mind that the necessary frictional forces for creating turbulence can be generated by rotating the outer body (hereafter alternatively referred to as "the housing") relative to the inner body instead of vice versa or by rotating the inner body and the housing in opposite directions.

The inner and outer bodies can be cylindrical or one or both of them may be of a diameter which varies along the axial length of such body or bodies, so that the annular space decreases in thickness towards the end thereof from which the mixed liquid materials discharge. Thus, the inner diameter of the housing may remain constant or decrease, while the external diameter of the inner body increases, or both said diameters may increase but at different rates, or the external diameter of the inner body may remain constant while the internal diameter of the housing decreases. Preferably however, the internal profile of the housing and the external profile of the inner body taper towards the discharge end.

The facing walls defining the layer space may be smooth or they may have a roughness and/or dot-like protuberances, which contribute(s) to creating the requisite turbulence. The turbulence can sometimes be promoted by designing or using the apparatus so that the liquid in the mixing passage is subjected to frictional forces, due to relative movement of the walls defining the layer space, which vary in magnitude and/or direction from one point to another along the liquid flow path. A change in circumferential velocity may occur abruptly if one or both bodies has or have a surface groove or grooves as hereinbefore referred to. More or less abrupt changes in angular velocity may be brought about by varying the speed of relative rotation of the bodies. In addition or alternatively, means may be provided for changing the direction of rotation of the inner body during the flow of any given quantum of liquid material along the annular passage, and/or the inner and/or the outer body may be oscillated in a direction parallel with the inlet-to-outlet flow direction.

Reference will hereafter be made to the accompanying drawings in which:

FIGS. **1** and **10** to **12** are diagrammatic cross-sectional views of continuous flow thin film reactors according to the invention;

FIGS. **2–3** show different types of rotors for the apparatus shown in FIG. **1**;

FIG. **4** is a cross-sectional elevation of a continuous flow film reactor of a type similar to that shown in FIG. **1**;

FIG. **5** shows a particular form of inlet system of use in the emulsification (precipitation) step in the preparation of a photographic silver halide emulsion when using mixing apparatus as shown in FIG. 4;

FIG. **6** is a block diagram representing an electronic measurement and control system for regulating the intake of photographic silver halide emulsion ingredients;

FIG. **7** is a flow diagram illustrating the continuous manufacture of light-sensitive silver halide coating compositions by means of mixing devices according to the invention;

FIGS. **8** and **9** are grain size distribution curves appertaining to silver halide dispersions prepared with the mixing apparatus illustrated in FIGS. **4** and **5**;

FIGS. **10** to **12** are diagrammatic cross-sectional elevations of three further mixing apparatus according to the invention, the parts being denoted by the same reference numerals as the corresponding parts in FIG. 1:

FIGS. **13** and **14** are graphs of the "turbidity-density" (D), measured spectrophotometrically, versus the wavelength, in nanometer (nm), for silver halide emulsion samples prepared with one embodiment of the present apparatus, illustrating the effect of variations in the pAg of such emulsions;

FIG. **15** is a graph similar to FIGS. **13** and **14** illustrating the effect of variation in the temperature during precipitation of the emulsion samples;

FIG. **16** is a further graph similar to FIGS. **13** and **14** showing the effect of ion concentration on the grain size of the silver halide emulsion;

FIG. **17** is another graph similar to FIGS. **13** and **14** showing the effect of pH on emulsion grain size;

FIG. **18** is a further graph similar to FIGS. **13** and **14** showing the effect of omitting a grain growth restraining agent during precipitation; and

FIG. **19** is a final graph similar to FIG. **18** showing the effect of two different grain growth restraining agents on the precipitation.

The mixing apparatus shown in FIG. **1** comprises a conical body **1** (rotor) rotatably driven by means of a shaft **2** connected to a suitable source of power such as an electrical motor. The rotor **1** rotates in a conical chamber **3**. The clearance designated (C) between rotor **1** and chamber **3** is variable by means of a regulating means comprising a threaded bolt **4**. The ingredients for forming a dispersion, e.g., by chemical reaction, emulsification, saltingout or crystallization are introduced through separate feed inlets, pipes or fittings **5**, into the hopper **6**, constituted by the upper portion of the apparatus. The formed mixture or reaction products are drained off through a pipe **7**.

The upper portion of the chamber **3** can be left open as shown, or it may be closed, optionally light-tightly, according to the necessities of the operation to be carried out.

The angles α and β as indicated in FIG. **1** need not necessarily be the same. The angle γ may vary, e.g., between 0° and 30°. The part of the rotatable body located within the hopper **6** need not necessarily have a conical shape.

The diameters ϕ_1 and ϕ_2 and the heights (h_1) and (h_2) are chosen according to the required mixing time and mixing degree of intensity. Laboratory scale models may have, e.g., rotors having a height of 20 cm and a diameter ϕ_1 of 10 cm. Large scale mixing apparatus for the mixing of rather large amounts of ingredients may have a rotor with a height of the order of 100 cm and a diameter ϕ_1 of the order of 50 cm.

The diameter ϕ_2 of the rotor at the drain off opening may be very small provided that the mechanical strength of the lower part of the rotor is sufficient and a proper balancing of the rotor is still possible.

The mixing apparatus according to FIG. **1** is normally operated in a vertical position so that gravity assists the flow of the liquid material to the outlet of the annular mixing passageway. However, the apparatus may be used in an inclined or even a horizontal position. In the latter case the rotor or rotating chamber preferably has a helical profile on its surfaces for conveying the mixture to the outlet.

Considering, e.g., the apparatus in vertical operation, the ingredients to be mixed in liquid phase are continuously fed at a controlled rate through the feed inlets **5** and continuously discharge into the annular mixing passageway between rotor **1** and chamber **3**. The liquid materials flow downwardly along a helical path within the said annular mixing passage-way under the combined action of gravity and the frictional forces on the liquid due to the high speed rotation of the rotor **1**. In the passage-way the liquid materials become thoroughly mixed by reason of the shearing forces which are generated throughout substantially the entire volume of the liquid in the passage-way, the whole of such liquid being in turbulent flow. Only very small quantities of liquids come into contact at any moment in the inlet end of the mixing passage-way and such quantities are constrained always to move away from that inlet end towards the discharge end. Consequently, in the case of precipitate-forming reactions, the reactants in those small quantities of liquids are substantially entirely used up in nucleation and not or not to any material extent in bringing about grain growth. The importance of the features referred to is apparent from the fact that in the preparation of a silver halide emulsion, if the reactants are fed at such a rate that they flow over and come into contact above the rotor rather than within the annular passage-way the result is an increase in the average grain size of the silver halide in the formed emulsion. It is to be understood that when using a rotor having no helical liquid conveying profile the rotation speed and the clearance between the rotor and the chamber have to be such that an effective friction and turbulent flow of the ingredients still takes place. That is why, in accordance with a preferred feature, the thickness of the annular passage between the chamber **23** and the rotor is made variable by the provision of the adjustment means **4.**

Referring to FIG. **1** it is self-explanatory that the rotor and the inner wall of the housing need not be conical and may have the shape of any other geometrical body of revolution having a decreasing diameter. The rotor body may, e.g., be shaped according to a curve forming part of a parabola, hyperbola or ellipse. In such cases the diameter of the rotor may still decrease from diameter ϕ_1 to diameter ϕ_2.

According to another embodiment, a rotor is used which is of generally conical form but has a helical peripheral groove, of constant or varying pitch. The crests and grooves may, e.g., be of conical, square, sinusoidal, semi-circular or any other required shape.

Two different forms of helically profiled rotors which can be used in a housing as illustrated in FIG. **1** are shown in FIGS. **2** and **3.** In the case of the rotor shown in FIG. **2** the rotor is formed with a helical groove the depth of which progressively diminishes towards the discharge end on the rotor while the diameter of the rotor, measured at the bottom of the groove remains constant. The rotor shown in FIG. **3** is of generally conical form with a taper towards the discharge end both along the crest of the thread and along the bottom of the thread groove. The angles of taper along the crests and along the bottom of the thread groove may be the same or different so that the depth of the helical groove remains constant or gradually varies as the case may be.

Instead of causing displacement of the liquids by rotating a rotor within a stationary chamber or housing, it is possible to make the liquids follow a helical course by rotating only the chamber or by rotating the chamber and the rotor in the same direction at different angular speeds or in opposite directions. For simplicity in construction and efficiency in mixing, it is preferable to use a device with a rotatable inner body and a stationary housing.

Further apparatus for use in carrying out the invention are shown in FIGS. **10, 11** and **12.** The elements indicated by the numbers **1, 2, 3, 6** and **7** have the same function as those denoted by those numerals in FIG. **1.**

In FIG. **4** a more detailed view is given of a laboratory mixing device, which is especially suitable for use in the continuous preparation of photographic silver halide emulsions. The rotor **1** is of threaded conical type. The chamber **3** surrounding the rotor is provided with a heating or cooling jacket **8** having an inlet **9** and outlet **10** for a heating liquid, steam or a coolant, according to the purpose in view. As an alternative an electrical heating means may be employed.

The clearance between chamber **3** and rotor **1** is variable by means of a centrally located threaded bolt **4** supporting a ballbearing **11** for the rotor. The rotor **1** is driven by means of an electrical motor **12** which is connected to a shaft **2** allowing for vertical adjustment of the rotor **1.** The mixing has a bottom outlet **7** and one or a plurality of inlet pipes **5** for the introduction of the ingredients to be mixed. The upper part **6** of the chamber is provided with a sensing device **13,** which may be of a pneumatic or electrical type. For example the sensing device comprises an electrically insulating tube containing two electrically conductive needles which make electrical contact with the liquid materials in the mixing device when they attain a predetermined level. The resulting electrical signal (control signal) is transmitted to the speed controller of gear pumps or other dosing means regulating the feed of the ingredients and/or is transmitted to the speed controller of the helically grooved rotor **1** to increase the rotor speed, so that the flow-through rate of the liquid materials is adjusted and the liquid does not rise above the said predetermined level.

The clearance between chamber **3** and rotor **1** is normally kept constant for one and the same mixing operation and can be adjusted taking into account factors such as viscosity, mixing effectiveness, reaction rate, heat transfer and volumes to be mixed in a certain period. The mixing effectiveness increases in inverse proportion to the clearance so that preference is given to so-called "thin-film" mixing wherein the mixing device operates with a clearance between the outermost surface parts of the rotor and the chamber wall of preferably about 0.5 mm in laboratory scale models (rotor height 20 cm) and of not more than 10 mm in large scale industrial models (rotor height 100 cm). The clearance is preferably variable between 0.01 and 10 mm.

In order to illustrate the use of apparatus according to the invention for continuous precipitation of silver halide in the preparation of photographic silver halide emulsions, reference is particularly made to FIGS. **5** and **6.**

In FIG. **5** a particular inlet system for silver halide precipitation is represented which system has to be considered as a modification of the inlet system represented in FIG. **4.**

According to FIG. **5** the inlet system contains three separate feed conduits **14, 15** and **16** provided with magnetic valves **17, 18** and **19** respectively. Apart from the inlet system the mixing apparatus is the same as that represented in FIG. **4** including a chamber jacket **8** for a heating or cooling gas or liquid, preferably steam or water. The dispersion formed in the mixing device discharges through the conduit **7** (FIG. **4**), which as indicated in FIG. **6** is provided with a thermometer and electrodes. The mixing apparatus is supported for operation in a vertical position by means of a supporting frame or mounting brackets (not shown).

An aqueous silver nitrate solution is fed at a controlled rate through conduit **14** and an aqueous solution of gelatin and water-soluble halide, e.g., potassium bromide and sodium chloride is fed at a controlled rate through the conduit **15.**

The conduit **16** is optionally used to introduce special ingredients or pH regulating compounds into the emulsification mixture. For example such conduit may be used to introduce an aqueous solution of ammonia or acetic acid and other substances that influence pH and grain growth.

The temperature of the reaction mass can be varied over wide limits according to the result aimed at, but is normally kept below 80°C, in the silver halide precipitation stage.

Gravity and/or pressure, e.g., air pressure, the speed of the rotor, the profile of the rotor and of the inner chamber wall, and the clearance between rotor and chamber wall, determine the time of passage through the mixing device.

Since the flow of the liquid mass in the annular passage-way around the rotor is highly turbulent a rapid contact between the reactants which are present in a thin liquid film and not in a bulky mass as in a batch process is ensured. Only very small quantities of reactants are allowed to come into contact at each moment. The products obtained discharge continuously and rapidly from the mixing device.

The silver halide formation is a fast chemical reaction and it proceeds continuously in such mixing device so that in a fairly short time large quantities of silver halide grains of reproducible quality are obtained.

The reactants are intimately mixed under conditions that permit excellent temperature control without the necessity of using a considerable excess of one of the reactants. The contact of small amounts of reactants in short contact time (e.g., from a fraction of a second to a few seconds) and the fast evacuation of the reaction products from the turbulent flow thin film mixing device makes it possible to produce silver halide emulsions with a narrow grain size distribution and very small grain size, e.g., a grain size below 100 nm and even below 30 nm.

In order to obtain highly reproducible results the silver halide precipitation can be electronically controlled and regulated by signals obtained in continuous measurement, as will be described with reference to FIG. **6.** The discharge pipe **7** of the thin film reactor is provided with a glass electrode **20** (pH-control), a silver electrode **21** (pAg control) and a common thermostabilized reference calomel electrode **22.** The latter electrode is connected to the emulsion flow by means of a saturated potassium nitrate bridge **23** containing the potassium nitrate, e.g., absorbed in agar-agar.

The potential difference between glass-electrode **20** and calomel-electrode **22** is fed to an electronic potentiometer **24** calibrated in pH-readings. The potential difference obtained between the silver electrode **21** and calomel-electrode is fed to an electronic potentiometer **25** yielding millivolt readings from which the pAg can be computed. The amounts of substances such as acetic acid and water-soluble halide for correcting the pH and pAg are controlled by magnetic valves **30** and **31** which are respectively connected to two process controllers **26** and **27** adjusted to maintain a given pH and pAg value respectively. The output of the potentiometers **24** and **25** is fed to said process controllers **26** and **27** and the difference signal is used to control the magnetic valves **30** and **31.** The electronic signals corresponding with the pH and pAg measurements are further fed to a recording galvanometer **32** so that a continuous diagram of the evolution of pH and pAg during precipitation is obtained.

The temperature, which has to be kept constant for obtaining reproducible results, can be measured at the outlet with a resistance thermometer and the output signal compared with a pre-set control signal in a differential potential transmitter. When the desired temperature conditions prevail, the difference between the two signals is zero. The difference signal is used, e.g., to control a needle valve on a steam supply inlet on the heating jacket of the conical mixing device or to control the speed of a motor connected to a gear pump which pumps a liquid coolant into the jacket. The outlet of the mixing apparatus may be additionally fitted with measuring means for measuring the turbidity, the spectral absorption and/or the conductivity of the passing liquid.

Apparatus according to the present invention can be applied in the preparation of all types of photographic emulsions, e.g., neutral, acid and ammonia type emulsions, and according to a pre-set programme adapted to different modes of emulsification. The manner of addition of the ingredients, the emulsification time, the emulsification temperature and the excess of halide present, either in uniform or decreasing amount, can be easily modified or varied. In considering emulsion formulae, the usual way of defining the quantity of halide is as the percentage excess over the quantity equivalent to silver. Iodobromide emulsions usually contain between 20 and 250 percent excess bromide during precipitation and ripening. Chlorobromide and chloride emulsions rarely contain more than about 10 percent excess halide and the excess may be as low as 1 to 2 percent in cases wherein very little grain growth is desired.

The quantity of ammonia, if any is used, may be introduced into the silver nitrate solution where its addition initially precipitates silver oxide, which on further ammonia addition dissolves to give a solution of complex amine. Alternatively, the ammonia may be incorporated in the halide/gelatin solution.

The pH of the precipitation mixture in case an ammoniacal emulsion is prepared is to a large extent controlled by the ammonia addition, but in other emulsions the pH during precipitation may be critical and has therefore to be kept carefully under control, notably with a view to preparation of small silver halide grains.

The proportion of the different halides in the silver halide crystal and their sequence of introduction can be easily controlled and, e.g., spread over two or more mixing devices arranged in series. So, it is easy to obtain types of composite grain emulsions, e.g., as described in the United Kingdom Patent Specification 1,027,146 filed Aug. 30, 1963 by Agfa AG.

According to the last mentioned process, a fine-grain emulsion with narrow grain size distribution is first prepared. After interruption of precipitation, chemical ripening is performed and precipitation is then continued. An emulsion comprising silver halide grains which consists of a chemically ripened core covered by an unripened layer of silver halide is obtained.

The turbulent flow mixing according to the invention in a thin film, is also suitable for the preparation of silver halide emulsions wherein a part or all of the silver halide of the initially formed silver halide grains is replaced (converted or substituted) by another type of silver halide, e.g., a silver chloride part is substituted by a bromide part, without changing the grain size. Such a type of silver halide emulsion is called "converted emulsion".

The cations of the halide used in the emulsion preparation are commonly potassium or ammonium but cations of alkaline-earth salts such as calcium chloride, or other soluble metal halides may be used. The latter may be introduced in either large or small quantities for special effects, e.g., cadmium ions are used for retarding the ripening of silver halide and to prepare contrasty silver chloride and silver chloro-bromide emulsions.

In order to restrain deliberately the grain growth, different measures can be taken. Thus, it is known that the silver halide grains formed during precipitation are finer at the minimum solubility of the silver halide, when the gelatin concentration is increased to a certain limit, when the temperature is above the gelling point of gelatin and preferably between 30°–40°C, or when crystallization nuclei such as silver iodide or silver sulphide are present.

Further it is possible to retard the crystal growth by means of chemical compounds selected from the group of e.g., imidazoles, thiazoles, thiolactic acid, 1-phenyl-5-mercapto-tetrazole, nucleic acids, thiosulphate, cystine, thioglycollic acid, and dithiopyrimidine. These grain growth inhibiting or retarding compounds may be added during the precipitation or added to the silver halide dispersion after its leaving of the turbulent flow mixing device. It is most significant that when forming a silver halide emulsion in a turbulent flow mixing device in accordance with the invention under conditions selected to promote the formation of fine grains the addition of a grain growth restrainer so that it is present in the mixing device appears to have little or no effect on the size of the silver halide grains in the emulsion discharging from the mixing device. It suffices therefore to add a restrainer to the emulsion as it leaves the mixing device.

Other grain growth restrainers that can be used are the mercaptotetrazole compounds referred to in United Kingdom Patent Specification 561,865 filed Dec. 3, 1942 by J. D. Kendall, the heterocyclic compounds or mercapto compounds described in in U.S. Pat. No. 2,432,506 of Leonard Vincent Chilton and Henry Phillips and 2,432,864 of Wifrid Hampden Dimsdale and Richard Robert Robinson, both issued Dec. 16, 1947, in French Patent Specification 1,557,289 filed Mar. 11, 1968 by Kodak and Co., Belgian Patent Specifications 710,602 filed Feb. 9, 1968 by Kodak and Co., and 723,492 filed Nov. 7, 1968 by Gevaert-Agfa N.V., and in the specifications of the United Kingdom Patent Applications 53,025/69 filed Oct. 29, 1969 and 54,539/69 filed Nov. 6, 1969 both by Gevaert-Agfa N.V., sulphonated heterocyclic mercapto compounds, e.g. 2-mercapto-5-sulphobenzothiazole, 2-mercapto-8-sulphonaphthoxazole and 2-mercapto-5-chloro-7-sulphobenzoxazole, selenium compounds, e.g. the diselenides described in the Belgian Patent Specification 747,012 filed Mar. 6, 1970 By Gevaert-Agfa N.V., e.g. diphenyl diselenide and p,p′-dichlorodiphenyl diselenide.

It is preferably to use grain growth restrainers containing aromatic nuclei.

The use of apparatus according to the invention in the preparation of silver halide emulsions, is of course not restricted to the preparation of fine grain emulsions. It is moreover possible and desirable for various purposes to ripen the emulsion discharging from the turbulent flow mixing passageway. This ripening can be performed without losing the advantage of a uniform emulsion with a narrow grain size distribution. In fact by physical ripening, the grain size distribution can be made even narrower.

A large grain size distribution can be obtained by carrying out the precipitation on already existing grains, e.g., by recycling the initially obtained grains or by carrying out further precipitation in one or more interconnected mixing devices through which the initially prepared emulsion is fed.

The flow diagram presented as in FIG. 7 shows the continuous production of light-sensitive silver halide emulsions using a series of thin film turbulent flow mixing devices according to FIG. 4.

The production starts with the precipitation of silver halide grains (emulsification) in a heatable and thermostabilizable mixing device **41** at a given temperature T_1. The said device is provided with two separate feed inlets **42** and **43**, one for the aqueous solution of the silver nitrate and one for the desired halide and protective colloid, usually gelatin. The feed proceeds at a rate controlled by magnetic valves **44** and **45** which are controlled by means of signals provided by the control, regulating and recording unit **46** which has been described in more detail in relation to FIG. **6**. This unit is connected to a resistance thermometer **47**, a glass-electrode **48**, a calomelelectrode **49** and a silver electrode **50**. The emulsion obtained in device **41** is introduced into device **51** in which the emulsion is subjected to a ripening treatment, at a temperature T_2 which is not necessarily the same as T_1; additional precipitation of silver halide on the already formed nuclei may take place; resulting in crystal growth. The inlet **52** with control valve **53** is used to introduce additional silver salts, halide and/or silver halide solvents or gelatin, e.g., phthaloyl gelatin.

The emulsion is optionally partly or wholly recycled through the conduit **54** provided with a regulating pump **55**.

At the conclusion of the physical ripening the gelatin is coagulated and co-precipitates with the silver halide in the mixing device **56**. For that purpose a suitable precipitant is introduced through the inlet **57** provided with control valve **58**. Thus, there can be used as precipitant an aqueous solution of ammonium sulphate, organic sulphonic acids, e.g. polystyrene sulphonic acid or simply a pH-decreasing substance in the event that acylated gelatin is added to the emulsion in the preceding step(s). The acylated gelatin is used in the emulsification stage or added at the conclusion of the ripening, which in the latter case is carried out above the isoelectric point of the gelatin. In the coagulation stage acid is introduced through inlet **57** to reduce the pH-value to about 4, whereupon the coagulation of the gelatin occurs. The coagulum, which preferably has the form of fine firm curds is applied to an endless belt **59** having a sieve-like character. A fine spray of wash-water is directed onto the curds, e.g. from a conduit **60** arranged along the whole length of the belt **59**. According to a particular embodiment a second and third washing may take place in a cooled mixing device of the type described in the present invention but having a sieve-like perforated chamber wall through which the washing liquids are evacuated.

At the conclusion of the washing stage the curds are fed into the hopper of a mixing device **61** and under intensive stirring at a proper temperature and pH the coagulum is redispersed therein. The pH-controlling compounds and water supplied at a proper temperature for the redispersion are introduced through the inlet **62** provided with a control valve **63**.

The redispersed silver halide crystals having obtained their final size distribution and being freed from impurities and excess halide ions, are now in a suitable condition for being mixed with chemical sensitizers in a mixing device **65** connected to mixing device **61** through outlet **64**.

In essence, the chemical sensitization consists in addition to the emulsion of chemical compounds which increase its lightsensitivity. The sensitization is associated with a special temperature treatment, usually performed after the addition of the sensitizer(s). This treatment at elevated temperature, e.g., from 40° to 75°C may last from a few minutes up to several hours, until the desired speed and maximal admitted fog are reached. The chemical sensitizer(s) are added at a controlled rate through the conduit **86** provided with a valve **87.** The outlet **66** of the mixing device **65** is directly or via an intermediate storage drum connected to a coil **69** positioned in a large thermostat **70** provided with the necessary temperature control unit **71** and stirring means **72.** The rate of passage of the emulsion through the coil determines the digestion time.

Three types of chemical sensitization are available for use in the digestion process according to the purpose in view:

1. sulphur sensitization,
2. reduction sensitization, and
3. precious metal sensitization.

At the conclusion of the chemical sensitization the necessary adjuvants for obtaining the photographic emulsion in its final form for coating are introduced through the conduit **75** fitted with valve **76** into the mixing device **74** and mixed therein with the silver halide emulsion introduced through conduit **73.** The emulsion ready for coating is discharged into the coating tray **77** in which the emulsion level is carefully controlled. The drawing represents a so-called trough coating method, by way of example, for coating a paper or film support **78,** which is guided by a guiding roller **79** and passes around a roller **80** so placed that the support **78** comes into contact with the surface of the emulsion **81,** which is kept at a closely controlled temperature.

In order to facilitate the transport of the photographic emulsion to and from the several mixing devices applied in its preparation the mixing devices are preferably arranged in cascade or assembled in a tower, analogously to a distillation tower, so that gravity helps in the feed of the emulsion from one device into another. By operating in light-tight vessels, only the washing and coating room have to be provided with the well known dark-room safe-lighting, so that a great deal of the processing can be carried out in normally lit operating rooms.

Apart from its use for the production of silver halide emulsions, apparatus according to the invention can be used in the preparation of all kinds of suspensions and emulsions by means of all types of physical or chemical reactions producing substances in particulate or droplet form in a liquid phase. For example the apparatus can be used for the preparation in turbulent flow conditions of all kinds of rather poorly water soluble salts or complexes, e.g., nickeldimethylglyoxime, $BaSO_4$, $PbCrO_4$, $ZnCrO_4$, CdS, ZnS, and other phosphors, e.g., suitable for fluorescent screens, metal oxides and hydroxides, e.g., HgO, $Pb(OH)_2$ $Fe(OH)_3$ and $Cr(OH)_3$ and metal particles, e.g. gold, mercury and silver dispersions obtained by reduction. The apparatus may also be used in salting out organic and inorganic compounds and in preparing polymer latices (aqueous polymer emulsions) and all kinds of colloid dispersions starting from colloid or polymer solutions.

As further examples of uses of apparatus according to the invention, it may be employed for preparing emulsions with very small droplets by feeding an emulsion containing larger droplets into the mixing passageway in which the turbulence prevails so that the droplets become divided by the action of the shearing forces which are generated through the whole volume of the liquid in the passageway. The formation of emulsions by mixing the materials which are to form the continuous and disperse phases in apparatus according to the present invention, or the use of that apparatus for reducing the droplet size of an emulsion previously prepared, is of special importance in the emulsification of colour couplers to be used in photographic materials, e.g. in the production of oil-in-gelatin emulsions wherein the disperse phase contains a dissolved colour coupler. The attainment of a narrow size distribution of the oil droplets is important for promoting uniform reaction of the coupler at all places in the photographic material and for producing images with low graininess. It has been found moreover that emulsions of oil-colour former in gelatin, prepared in apparatus according to the invention in its preferred embodiments, are not opalescent but form layers that are completely transparent in the dry state. In addition the layers are much more resistant than layers prepared from the customary emulsions, to spoiling by folding. This is due to the very good elasticity of the layers. Another specific example of the use of this invention, it can be employed for preparing dispersions of barium sulphate in a protective colloid for forming coating layers on paper and other types of support.

Moreover the mixing device according to the present invention may be used, e.g., in the preparation of paints, varnishes, lubricants, cosmetic products, pharmaceuticals, alimentary substances, e.g., fats, oils and emulsions thereof. Further it may be used as a continuous flow thin film reactor for, e.g., chemical processes such as salt formation by precipitation, nitration, sulfonation, diazotation, coupling, hydrolysis, alkylation, Friedel-Crafts reactions, acylation, esterification and polymerization. According to a particular embodiment the mixing vessel is also suited for mixing liquids with gases, e.g., under pressure, and to allow to react liquids with gases, e.g., in chemical processes such as halogenation, amination by reduction, amination by ammonolysis, oxidation and hydrogenation. According to a particular embodiment the gases are introduced through openings provided in the rotor wall.

Proper temperature control is very easy since no large reaction masses come into contact with each other and the reactants reach each other in the thin liquid film in reproducible concentrations. Therefore the mixing apparatus of the present invention can also be used for the continuous melting of gels as, e.g., the noodles of a photographic gelatino-silver halide emulsion.

When using the apparatus for chemical reactions the reaction mass can be recycled through the mixing device or sent through a battery of mixing apparatus arranged in series.

The mixing device according to the present invention is particularly suited as reaction vessel for chemical reactions in different non-miscible liquid phases also known as interfacial reactions. Polycondensation polymers, polyamides and polyesters can be prepared according to an interfacial condensation technique.

The use of apparatus according to the present invention is illustrated by the following Examples.

EXAMPLE 1

The following four solutions were prepared separately:

A. an aqueous ammoniacal silver nitrate solution containing per litre 3/3.5 mole of silver nitrate and 6/3.5 mole of NH_4OH;
B. an aqueous halide solution containing 3 mole of potassium halide per liter (KBr/KCl/KI - 100/10/1 parts by weight);
C. an aqueous acetic acid solution containing 3.5 mole of CH_3COOH per liter;
D. an aqueous 0.5 percent by weight gelatin solution.

Starting from said solutions the precipitation (emulsification) of light-sensitive silver halide was carried out in a mixing vessel with an inlet system according to FIG. **5** and having a housing and rotor as diagrammatically represented in FIG. **4.**

The height h_1 (see FIG. **1**) of the rotor part in the conical chamber was 122 mm. The height h_2 of the rotor part in the hopper was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm. The angles α and β were both 10°. The clearance (c) was 1.5 mm.

The rotor was formed with a rectangular section helicoidal groove.

The width of the groove between the crests of the thread was 7 mm, the width of the crests 3 mm and the depth of the groove 1.5 mm. The rotor and light-tight housing were made of stainless steel. The angular speed of the rotor during the precipitation was 760 rpm. The solutions (A), (B), (C) and (D) were simultaneously introduced in the following proportions through the separate inlets **14, 15, 16** and **29** as indicated in FIG. **5.**

Solution (A) ; 174 ml per min.
Solution (B) ; 148 ml per min.
Solution (C) ; 82 ml per min.
Solution (D) ; 280 ml per min.

Working under these conditions the contact time of the reactants in the clearance (thin film) was about 2.5 sec.

The temperature was kept constant at 49°C during the precipitation. The pH and pAg expressed in mV measured at the outlet were 8.15 and −35 mV respectively. Immediately after the dispersion leaves the mixing vessel, its pH was reduced to 5.00.

The apparatus was kept in operation under the above described working conditions for 16 min.

The mean diameter of the silver halide grains obtained was 114 nm. The mean diameter of the grain was determined by means of specific adsorption of a dye as described in Photographische Korrespondenz Band 101, Nr. 3 (1965), p. 38–39 and by electron microscopic measurement.

From the grain size distribution curve presented as FIG. **8** it is apparent that the distribution is very narrow. The ordinate of the diagram stands for increasing grain diameters expressed in nanometer (*nm*). The abscissa of the diagram stands for the number (N) expressed as a percentage of grains having a diameter smaller than the value corresponding therewith on the ordinate. The graph shows that 98 percent of the grains have a grain size between 50 and 300 nm.

EXAMPLE 2

This example relates to the preparation of a photographic silver halide emulsion with large grain size distribution by plural stage treatment.

The following solutions were prepared for use in a first precipitation stage.

A. a mixture of 1.5 parts of volume of ammoniacal silver nitrate containing per liter 3 mole of silver nitrate and 6 mole of ammonium hydroxide and 3.5 parts by volume of demineralized water,
B. a homogeneous mixture of:

a 3 molar aqueous solution of potassium bromide	4000 ml
a 3 molar aqueous solution of sodium chloride	300 ml
a 3 molar aqueous solution of potassium iodide	100 ml
demineralized water	2700 ml
inert gelatin	300 g
sufficient aqueous ammonium hydroxide to reach a pH of 10.5 measured at 30°C.	

First Precipitation Stage

A mixing device **1** of the type described in Example 1 was used and the solution (A) and (B) were introduced therein through separate inlets at a rate of 65 ml per min. and 300 ml per min. respectively.

During the precipitation the angular speed of the rotor was 500 rpm.

The temperature measured at the outlet was 62°C.

The pH and pAg expressed in mV and measured at the outlet were respectively 10.8 and −160 mV. The first precipitation operation lasted 3 min.

Second Precipitation Stage

In the same mixing device as used in the first precipitation stage the following liquids were introduced through separate inlets at the specified rates:

liquid (A) as used in precipitation stage 1 at a rate of 65 ml per min.
liquid (B) as used in precipitation stage 1 at a rate of 300 ml per min.
the dispersion discharging from the mixing device in precipitation stage 1, at a rate of 500 ml per min.

The duration of the second precipitation operation was **2** min.

Third Precipitation Stage

The precipitation stage 1 was repeated with the difference, however that now the output dispersion of precipitation stage 2 was used in combination with the solutions (A) and (B) of stage 1.

The introduction rates were:
solution (A) ; 65 ml per min.
solution (B) ; 300 ml per min.
Output dispersion of precipitation stage 2:500 ml per min.

The mean diameter of the silver halide grains obtained was 300 nm. The mean diameter was measured by an electron microscope.

The results are represented in FIG. **9** from which it can be seen that 98 percent of the grains have a grain size between **10** and 1000 nm. The ordinate of the graph stands for increasing grain diameters expressed in nanometer (nm). The abscissa of the diagram stands for the number N (expressed as a percentage) of grains having a diameter lower than that indicated by the corresponding "nm" value.

EXAMPLE 3

The following four solutions were prepared separately:

A. an aqueous solution containing per liter 0.3 mole of silver nitrate,
B. an aqueous halide solution containing 0.3 mole of potassium bromide per liter,
C. an aqueous acetic acid solution containing 3.5 mole of CH_3COOH per liter,
D. an aqueous 1 percent by weight gelatin solution.

Starting from said solutions the precipitation (emulsification) of light-sensitive silver bromide was carried out in a mixing vessel with an inlet system according to FIG. **5** and having a housing and rotor as schematically represented in FIG. **4.**

The height h_1 (see FIG. **1**) of the rotor part in the conical chamber was 122 mm. The height h_2 of the rotor part in the hopper was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm.

The angles α and β were both 10°. The clearance (c) was 1.5 mm.

The rotor was formed with a rectangular section helicoidal groove.

The width of the groove between the crests of the thread was 7 mm, the width of the crests 3 mm and the depth of the groove 1.5 mm.

The rotor and light-tight housing were made of stainless steel.

The angular speed of the rotor during the precipitation was 900 rpm.

The solutions (A), (B), (C) and (D) were simultaneously introduced in the following proportions through the separate inlets **14, 15, 16** and **29** as indicated in FIG. **5.**

Solution (A):193 ml per min.
Solution (B):164 ml per min.
Solution (C):58 ml per min.
Solution (D):700 ml per min.

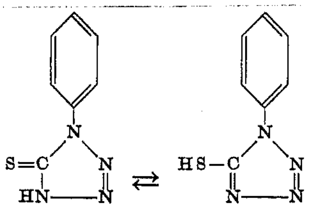
Working under these conditions the concentration of the silver ions potentiometrically measured at the outlet of the mixing device is such that it is between + 300 and + 400 mV and the pH is between 3 and 4. The contact time of the reactants in the clearance (thin film) was about 2.5 sec.

The temperature was kept constant at 35°C during the precipitation.

The dispersion leaving the outlet was mixed with an aqueous potassium bromide solution at such a rate that a voltage of +50 mV was potentiometrically measured in the mixed composition.

The mean diameter of the silver halide grains obtained at the outlet was 100 nm. The mean diameter of the grains was determined turbidimetrically as described in Scientific and Industrial Photography (2) vol. 19, November 1948, pages 401–418 and by measurement with an electron microscope.

When using 300 mg of 1-phenyl-2-tetrazoline-5-thion having the following tautomeric structures:



per mole of silver nitrate as grain growth restrainer in solution (B) and operating under the conditions above described silver bromide grains having a mean diameter of 20 nm were obtained.

EXAMPLE 4

Barium sulphate was prepared by precipitation using an apparatus like that used in Example 3, but having a rotor without a helical peripheral groove.

Two liquids (P) and (Q) were separately introduced into the clearance between the rotor and the housing.

(P) an aqueous 1 molar sulphuric acid solution,
(Q) an aqueous 1 molar barium chloride solution.

The feed rate of liquids (P) and (Q) was 100 ml in 24 sec. and 100 ml in 25 sec. respectively. The liquids were fed into the clearance tangentially to the rotor surface and in the direction of the rotor rotation. The clearance was 1.7 mm, the temperature 20°C and the rotor speed 815 revolutions per minute.

In order to compare the difference in grain size between barium sulphate prepared from the same solution in a batch process, i.e., in e vessel provided with helical stirrer, and the barium sulphate prepared in this example, the sedimentation rates of the barium sulphate in the sample of the different suspensions were compared.

The batch process sample inspected in a sedimentation tube had a sedimentation time of 15 min. The sample prepared in the continuous process according to the invention had a sedimentation time of 95 min. for the same degree of sedimentation (1 cm of clear liquid at the top of the column).

EXAMPLE 5

A dispersion of ethylcellulose in an ethanol-water mixture was prepared in a mixing device as diagrammatically illustrated in FIG. **1.** The height (h_1) of the rotor part in the conical chamber was 122 mm. The height (h_2) of the rotor part in the hopper was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm. The angles α and β were both 10°. The rotor was made of stainless steel and had a smooth surface.

Two starting liquids, viz. water and a 5 % by weight solution in ethanol of Ethylcellulose N7 (trade name of The Hercules Powder Company Inc. for an ethylcellulose insoluble in a mixture of water and ethanol (1:1 by volume)) were separately introduced into the clearance between the rotor and the housing.

The rotor speed was 930 rpm, the clearance 0.44 mm, and the temperature of the liquids 20°C.

The water was introduced at a rate of 104 ml per min. and the ethylcellulose solution at 14 ml per min.

A batch process operating with high speed stirrer (mixing turbine impeller), using the same liquids in the same volume ratio, yielded a much coarser dispersion than that obtained by means of the continuous turbulent flow mixing device according to this example.

EXAMPLE 6

The following four solutions were prepared separately:

A. an aqueous solution containing 0.3 mole of silver nitrate per liter,
B. an aqueous halide solution containing 0.3 mole of potassium bromide per liter,

C. a 20 percent aqueous acetic acid solution,

D. an aqueous 1 percent by weight gelatin solution.

Starting from said solutions the precipitation (emulsification) of light-sensitive silver bromide was carried out in a turbulent flow mixing vessel with an inlet system according to FIG. **5** and having a housing and rotor according to FIG. **4**.

The height h_1 (FIG. **1**) of the rotor part in the conical chamber was 122 mm. The height of the rotor part in the hopper was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm. The clearance (C) was 1.5 mm. The pitch of the thread on the rotor was **6** mm. The depth of the groove was 2 mm. The width of the groove between the crests of the thread was 6.5 mm.

The rotor and the light-tight housing were made of stainless steel.

The angular speed of the rotor during the precipitation was 850 rpm.

The solutions (A), (B), (C) and (D) were simultaneously introduced through the separate inlets **14, 15, 16** and **29,** as indicated in FIG. **5.**

Solution (C) was introduced at such a rate that at the outlet of the apparatus a pH of 3.5 was obtained in all tests as described hereinafter.

Solution (D) was introduced at a rate of 600 ml per min. in all tests as described hereinafter.

The following Table 1 gives data appertaining to sixteen different tests to show the evolution of the silver halide grain size as a function of the pAg measured at the outlet of the turbulent flow mixing vessel. The pAg values and density (D) values corresponding with the turbidity of the dispersions were measured at 750 nm 1.5 min. after the emulsion left the mixing apparatus. The measurement was made in spectrophotometer cells of a spectrophotometer known as the "Spectronic 505" (trade mark of Bausch and Lomb Inc., Rochester, N.Y., U.S.A.).

The turbidity-density is directly proportional to the grain size of the precipitated silver halide.

The silver nitrate solution (solution A) and the potassium bromide solution (solution B) were introduced, when operating in an equimolar ratio, at a rate of 152 ml per min. The temperature maintained during the precipitation was 35°C.

TABLE 1

Test No.	pAg	Density (D)
1	2.75	0.31
2	3.15	0.30
3	3.65	0.34
4	4.00	0.39
5	4.35	0.51
6	4.70	0.47
7	4.85	0.84
8	5.60	0.46
9	5.85	0.43
10	10.00	0.50
11	9.20	0.33
12	8.50	0.31
13	7.80	0.40
14	7.40	0.44
15	6.50	0.52
16	6.30	0.52

FIGS. **13** and **14** are graphs obtained by plotting the "turbidity-density" (D) versus wavelength (from 760 to 600 nm) in respect of the tests 1–16. The curves 1–9 of FIG. **13** correspond with tests 1–9 of the preceding table, and the curves 1–7 of FIG. **14** with the tests 10–16 of said table.

It can be seen from these curves that in the range of low pAg-values, i.e., from 2.75 to 6, the turbidity, in other words the mean grain size, is minimal at the pAg value at which the silver halide solubility is also minimal (pAg = 3.00).

In the range of higher pAg values 10 to 6 due to excess of halide ions in respect of silver ions the turbidity is minimal at pAg = 8.5.

EXAMPLE 7

The same procedure as explained in Example 6 was followed for a pAg of 7.9 (= 85 millivolt) at a temperature of precipitation of 35° and 42°C respectively.

In FIG. **15** curves **1** and **2** represent the relationship of "turbidity-density" (D) to wavelength (nm) in respect of silver bromide dispersions formed at 35° and 42°C respectively. From these curves it can be seen that grain size of the silver bromide increases directly proportionally to the temperature of precipitation.

EXAMPLE 8

The following four solutions were prepared separately:

(A) aqueous solution containing 0.3 mole of silver nitrate per liter,

(B) aqueous halide solution containing 0.3 mole of potassium bromide and 2 percent by weight of gelatin,

(C) 20 percent aqueous acetic acid solution,

(D) aqueous 1 percent by weight gelatin solution.

Starting from these solutions the precipitation (emulsification) of light-sensitive silver bromide was carried out in a turbulent flow mixing vessel as described in Example 6.

During the precipitation, the angular speed of the rotor was 850 rpm.

The curves **1** and **2** in FIG. **16** give an indication of the effect of the silver ion and halide ion concentrations on the silver halide grain size.

At the start of the precipitation these concentrations may be easily controlled by regulating the supply of solution (D) which acts as a diluent.

The operating conditions for two tests were chosen in such a way that in a first test the silver nitrate and potassium bromide came into contact inside the mixing vessel in concentrations of 0.05 mole/liter, while in a second test the concentrations on such contact were 0.075 mole/liter. This was realized by introducing the silver nitrate solution (A) and potassium bromide solution (B) in equimolar amounts at a rate of 152 ml per min. and introducing liquid (D) at a rate of 600 and 300 ml per min. for tests 1 and 2 respectively. During this operation the pH was kept at 3.5 by means of solution (C).

The temperature during the precipitation was maintained at 35°C.

Samples of the emulsion discharged from the mixing device were taken 1.5 min. after the precipitation and the turbidity thereof was measured as described in Example **6.**

Curve **1** of FIG. **16** represents the turbidity-density (D) versus wavelength (nm) variation of the sample obtained in test 1 wherein per liter 0.05 mole of silver nitrate and 0.05 mole of potassium bromide were used in the precipitation stage.

From the curves in FIG. **16** it can be deduced that with a rise in the concentration of the starting materials (silver ions and halide ions) the grain size of the silver halide increases and that by using a low concentration solution, i.e., a solution containing per liter about 0.05 mole of each of the reagents, very fine grains can be obtained under the conditions described.

The mean grain sizes of the silver halide grains obtained in tests 1 and 2 were 11 nm and 26 nm respectively.

EXAMPLE 9

The following four solutions were prepared separately:

A. an aqueous solution containing 0.3 mole of silver nitrate per liter,

B. an aqueous solution containing 0.3 mole of potassium bromide and 2 percent by weight of gelatin,

C. a 20 percent aqueous acetic acid solution,

D. an aqueous 1 percent by weight gelatin solution,

E. as pH-correcting solution, a **1N** aqueous sodium hydroxide solution,

F. as pAg-correcting solution, an aqueous solution of 0.03 mole of silver nitrate per liter.

Starting from said solutions the precipitation (emulsification) of light-sensitive silver bromide was carried out in a turbulent flow mixing vessel as described in Example 6.

During the precipitation the angular speed of the rotor was 850 rpm.

The curves **1** and **2** in FIG. **17** give an indication of the effect on the silver halide grain size of the pH, at a constant pAg-value of 2.75.

In a first test (represented by curve **1**) the precipitation was carried out at a pH-value 3.5 and in a second test (represented by curve **2**) the precipitation was carried out at a pH-value of 5.0.

Samples of emulsion discharged from the mixing vessel were taken 1.5 min. after the precipitation, and the turbidity thereof was measured as described in example 6.

Curve **1** of FIG. **17** represents the turbidity-density (D) versus wavelength (nm) variation of the product of the first test, which was obtained operating at a pH-value 3.5.

Curve **2** of FIG. **17** represents the turbidity-density (D) versus wavelength (nm) variation of the product of the second test, which was obtained operating at a pH-value 5.0.

From the curves in FIG. **17** can be deduced that with a rise in the pH-value the grain size of the silver halide increases.

The average grain sizes of the silver halide grains obtained in the first and second test were 11 nm and 36 nm respectively.

EXAMPLE 10

The following four solutions were prepared separately:

A. an aqueous solution containing 0.3 mole of silver nitrate,

B. an aqueous halide solution containing 0.3 mole of potassium bromide per liter and 2 percent by weight of gelatin,

C. a 20 percent aqueous acetic acid solution,

D. an aqueous 1 percent by weight gelatin solution.

Starting from these solutions the precipitation (emulsification) of light-sensitive silver bromide was carried out in a turbulent flow mixing vessel with an inlet system according to FIG. **5** and having a housing and rotor as shown in FIG. **1**.

The height h_1 (see FIG. **1**) of the rotor part in the conical chamber was **122** mm. The height of the rotor part in the hopper was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm. The clearance (C) was 1.5 mm.

The rotor and the light-tight housing were made of stainless steel.

The angular speed of the rotor during the precipitation was 800 rpm.

The solutions (A), (B), (C) and (D) were simultaneously introduced through the separate inlets **14, 15, 16** and **29** as indicated in FIG. **15.**

Solution (C) was introduced at such a rate that at the outlet of the apparatus a pH ov 3.5 was obtained in all tests as described hereinafter.

Solution (D) was introduced at a rate of 600 ml per min. in all of the tests as described hereinafter. The millivolt reading at the outlet was 420 mV. Immediately after the silver halide dispersion left the apparatus, sufficient aqueous potassium bromide solution was added to bring the millivolt value at 50.

In test 1, which is here the reference test, no grain growth restrainer was used during the precipitation.

In test **2** 1 ml of 20 percent aqueous solution of poly-N-vinylpyrrolidone were added as grain growth restrainer per 100 ml of emulsion leaving the apparatus.

In FIG. **18** curves **1, 3** and **4** represent the turbidity-density (D) variations versus wavelength (nm) of a sample of the product of test 1 taken off 1.5 min., 10 min. and 20 min. respectively after the silver halide dispersions left the mixing vessel. Curve **2** represents the turbidity-density (D) variations wavelength (nm) of a sample of the product of test 2 taken 1.5 min. leaving the mixing vessel. The turbidity was measured by means of a spectrophotometer known as the "Spectronic 505" as referred to in example 6.

EXAMPLE 11

The following four solutions were prepared separately:

A. an aqueous solution containing 0.3 mole of silver nitrate per liter,

B. an aqueous solution containing 0.3 mole of potassium bromide and 2 percent by weight of gelatin,

C. an aqueous acetic acid solution,

D. an aqueous 1 percent by weight gelatin solution.

Starting from these solutions the precipitation (emulsification) of light-sensitive silver bromide was carried out in a turbulent flow mixing vessel as described in Example 6.

During the precipitation the angular speed of the rotor was 900 rpm.

The solutions (A), (B), (C) and (D) were simultaneously introduced through the separate inlets **14, 15, 16** and **29** as indicated in FIG. **5.**

Solution A was introduced in a ratio of 190 ml per min.

Solution B was introduced in a ratio of 160 ml per min.

Solution C was introduced in a ratio of 70 ml per min.

Solution D was introduced in a ratio of 700 ml per min.

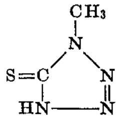
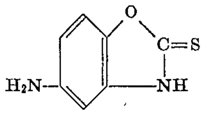
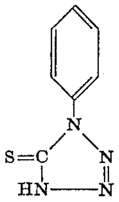
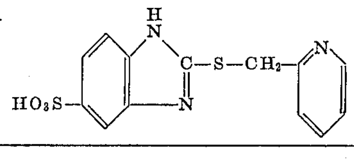
A series of tests was carried out wherein immediately after the silver halide dispersion left the mixing vessel, 0.5 millimole of a grain growth restrainer was added and the dispersion was adjusted by means of aqueous potassium bromide solution to a millivolt reading of + 50 mV (Ag/saturated calomel electrode).

Samples of the emulsion of the different tests were then treated under the same conditions with an aqueous 20 percent by weight ammonium sulphate solution and with the precipitated gelatin-surrounded silver halide washed with 5 liter of demineralized water containing 0.25 millimole of the particular grain growth restrainer used at the end of the emulsification stage.

The whole operation of precipitating the emulsion grains and washing them lasted 1 h 30 min. Before taking samples and making photographs of the silver bromide grains in an electronic microscope (enlargement 50,000 ×) each sample was kept at 40°C for 2 h.

In the following table II are listed the grain growth restrainer used and the average silver bromide grain size obtained in the different tests.

TABLE II

Test No.	Grain growth restrainer	Average grain size, nm.
1		60
2		40
3		30
4		22
5		18

In FIG. 19 curve 1 represents the turbidity-density (D) versus wavelength (nm) variation of a sample prepared under the running conditions of test 1 and taken 1.5 min. after leaving the outlet of the mixing vessel. Curve 2 represents the turbidity-density (D) versus wavelength (nm) variation of a sample prepared and taken under the running conditions of test 4 1.5 min. after leaving the outlet of the mixing vessel.

EXAMPLE 12

The following liquids (A) and (B) were prepared for separate introduction into a mixing device as diagrammatically illustrated in FIG. 1.

A. a 10 percent by weight aqueous gelatin solution,

B. dibutyl phthalate.

The height (h_1) of the rotor part in the conical chamber was 122 mm. The height (h_2) of the rotor part in the hopper was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm. The angles α and β were both 10°. The clearance (C) during the operation was 0.87 mm. The rotor was made of stainless steel and had a smooth surface. The rotor speed was 1,000 rpm.

Liquids (A) and (B) were introduced into the clearance at the top through the separate inlets. Liquid (A) was introduced at a rate of 700 ml in 3 min 55 sec, while liquid (B) was introduced at a rate of 8.4 ml in the same time.

The temperature of the liquids in the mixing zone was 40°C. The liquid obtained at the outlet was re-fed once into the mixing device through one of the inlets.

The obtained emulsion was coated on a subbed cellulose triacetate support at a rate of 12.5 g of gelatin per sq.m.

Tests carried out on brittleness showed that the emulsion layer has a much better resistance to spoiling by folding than layers that did not contain the dibutyl phthalate droplets.

The gelatin layer containing the oil droplets was completely transparent in dry state. Similarly good results were obtained with dimethyl phthalate. A higher content of dibutyl phthalate or dimethyl phthalate by introducing said liquids at rates of 11.2 ml and 14 ml per 3 min. 55 sec resulted in gelatin coatings with still better elasticity.

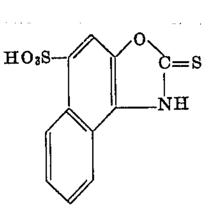
This example gives an indication of how according to the invention a colour coupler can be distributed in an oil in a colloid binder. It is merely necessary to dissolve the selected colour coupler in the oil used for forming the disperse phase of the emulsion.

EXAMPLE 13

The following four solutions were prepared separately:

A. an aqueous solution containing 0.3 mole of silver nitrate per liter diluted with 5 times its volume by distilled water,

B. 500 ml of an aqueous solution containing 0.3 mole of potassium bromide, 16 g of gelatin, 2,484 ml of distilled water, 1,000 ml of ethanol and 10 g of a grain growth restrainer having the following formula:



C. a diluted aqueous acetic acid solution,

D. an aqueous solution containing 3,200 ml of water, 800 g of gelatin and 5 g of the above-mentioned grain growth restrainer.

By starting from these solutions the precipitation (emulsification) of light-sensitive silver bromide was carried out in a turbulent flow mixing apparatus as diagrammatically represented in FIG. 1 but wherein the solutions A and D were introduced at the centre of the conical rotor part in the hopper and the solutions B and C were introduced by spraying them against the inner wall of the hopper.

The characteristic measures of the mixing apparatus were the following:

$h_1 = 91$ mm
$h_2 = 45$ mm
$\phi_1 = 42$ mm
$\phi_2 = 6$ mm

The clearance (C) was 1.2 mm and the angular speed of the rotor during the introduction of these aqueous solutions was 1150 rpm.

The solutions (A), (B), (C) and (D) were introduced at a rate of 200, 205, 150 and 190 ml per min. respectively.

The pH was kept thereby at 3.2 and the millivolt reading at the outlet being a measure for the pAg was + 440 mV when operating at a precipitating temperature of 38°C.

After precipitation the millivolt reading was adjusted at 70 mV by mixing the precipitate composition with aqueous potassium bromide.

Samples taken from the thus treated precipitate contained a major part of silver halide grains having a size of 5 nm.

EXAMPLE 14

A modified apparatus of the type diagrammatically represented in FIG. 4 was used for melting silver halide emulsion noodles (a silver halide emulsion in gel-state).

The apparatus contained no inlet system as schematically represented in FIG. 5 but the hopper was left open and served as a large feed pipe into which the noodles were introduced.

The height (h_1) (see FIG. 1) of the rotor part in the conical chamber was 122 mm. The height of the conical rotor part in the hopper was 65 mm.

The height (h_2) of hopper was 150 mm and its diameter was 80 mm.

The diameter ϕ_1 of the rotor was **54** mm and the diameter ϕ_2 was 5 mm.

The clearance (C) was 0.8 mm. The rotor surface was helicoidally grooved with two parallel grooves. The pitch of the threads was 6 mm. The depth of the grooves was 3 mm and the width of each groove 6.5 mm.

The noodles were introduced at 14°C and the temperature of the housing surrounding the rotor was kept at 45°C. The angular rotor speed was 500 rpm. The introduction of the noodles proceeded at such a speed that the hopper was kept filled during the operation of the apparatus.

The gelatino-silver halide emulsion left the apparatus in sol-state at 37°C.

EXAMPLE 15

The following two solutions were prepared separately:

A. a solution of 150 g of polymethyl methacrylate dissolved in 750 ml of ethyl acetate.
B. a solution of 300 g of gelatine dissolved in 2,100 ml of water containing 24 ml of a 20 percent by weight aqueous solution of the dispersing agent MERSOLAT (trade name for a sulphonated paraffine of Bayer A. G. Leverkusen, W-Germany).

Said solutions A and B were introduced simultaneously in the annular passage of a mixing vessel having a housing and rotor as diagrammatically represented in FIG. 4.

The height h_1 (see FIG. 1) of the rotor part in the conical chamber was 122 mm. The height h_2 of the rotor part in the hopper was 65 mm. The diameter ϕ_1 of the rotor was 54 mm and the diameter ϕ_2 was 5 mm. The angles α and β were both 10°. The clearance (C) was 1.7 mm.

The rotor had a smooth surface and the rotor and light-tight housing were made of stainless steel.

The angular speed of the rotor during the mixing was 1030 rpm.

The solutions (A) and (B) were introduced in the following proportions:

Solution (A):70 ml per min.
Solution (B):92 ml per min.

Working under these conditions the contact time of the reactants in the clearance (thin film) was about 2.0 sec.

The temperature was kept constant at 44°C during the dispersing.

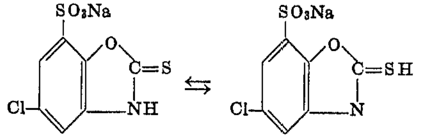
The mean diameter of the dispersed polymethyl methacrylate particles was 5000 nm. The mean diameter of the particles was determined by microscopic measurement.

The particle size distribution of the globules obtained by this procedure was much more homogeneous than could be obtained in a batch process dispersing technique. Moreover, the present continuous flow thin film mixing process allows the use of much more concentrated polymer solutions and the use of less dispersing agent and gelatine as protective colloid.

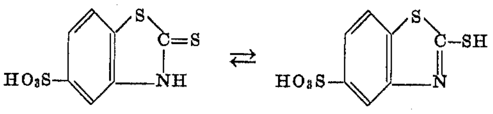
EXAMPLE 16

Example 13 was repeated but using a same amount of grain growth restrainer according to one of the following structural formulae:

1.



2.



Silver halide grains produced in the presence of such a grain growth restrained had an average grain size of 5 nm.

We claim:

1. A continuous flow liquid mixing apparatus which comprises a central inner rotor and an outer housing surrounding the peripheral surface of the rotor, said housing and rotor being arranged coaxially to define therebetween a clearance space in the form of an annular passage having a cross-section continuously and gradually decreasing in radial dimension, said annular passage serving as a mixing zone having an inlet opening at the larger end thereof and an outlet opening at the smaller end thereof, the mutually facing peripheral walls of said rotor and housing defining said annular passage being continuous and smooth and free of interruptions or perforations, means for imparting to said rotor and housing relative rotational movement about

their axis to apply shearing forces to the liquid flowing through said mixing zone, the mutually facing peripheral wall sections of said rotor and housing diverging sharply in the region upstream of said mixing zone inlet opening and being free of interruptions, and means for introducing at least one liquid to be mixed into said upstream region whereby all such liquids are introduced uniformly and homogeneously into said mixing zone.

2. An apparatus according to claim **1** wherein the housing extends above said rotor generally parallel to the axis of revolution and said rotor tapers inwardly toward said axis to define said sharply diverging wall sections.

3. An apparatus according to claim **1** wherein the internal periphery of the housing and the external periphery of the rotor taper towards said outlet opening.

4. An apparatus according to claim **3** wherein the internal periphery of the housing and the external periphery of the rotor are conical.

5. An apparatus according to claim **1** wherein the rotor is arranged for rotation and the housing is nonrotatable.

6. An apparatus according to claim **5** wherein the rotor has an axially extending shaft by means of which it can be coupled to a motor.

7. An apparatus according to claim **5** wherein the upper end of said rotor has a generally inverted conical shape.

8. An apparatus according to claim **1** wherein said axis is vertical.

9. An apparatus according to claim **1** wherein the maximum annular radius in said mixing zone is 10 mm.

10. An apparatus according to claim **9** wherein the maximum annular radius is not more than 5 mm.

11. An apparatus according to claim **1** wherein the mean diameter of the annular passage defining said mixing zone in any plane normal to the axis of relative rotation of the rotor and housing is substantially less than the axial length of said zone measured from the inlet to the outlet openings thereof.

12. An apparatus according to claim **11** wherein the axial length of the mixing zone is at least 1.25 as large as its mean diameter.

13. An apparatus according to claim **1** wherein the clearance between the inner wall of the housing and the outer wall of the rotor is from 10 mm to 0.01 mm.

14. An apparatus according to claim **1** wherein a plurality of inlet pipes terminate in the sharply divergent region of said rotor and housing walls to introduce plural liquids to be mixed.

15. A continuous flow liquid mixing method which comprises the steps of:

a. passing at least one liquid to be mixed through a mixing zone having the form of an annular passage defined between the mutually facing peripheral surfaces of a housing and a rotor arranged coaxially within the housing, said surfaces being continuous and smooth and free of interruptions or perforations, said zone gradually and continuously decreasing in radial cross-section from an inlet opening to an outlet opening, and

b. imparting relative rotational movement to the surfaces defining said zone at a speed sufficient to create a turbulent flow condition in the liquid passing through said zone.

16. The method according to claim **15** wherein the mutually facing surfaces of said housing and rotor diverge sharply upstream of said mixing zone to define a feeding zone free of interruptions or obstructions and including the step of supplying plural liquids to be mixed into said feeding zone.

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