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Johnson et al.

[11] **3,850,643**

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[54] **PROCESS FOR MAKING COUPLER DISPERSIONS**

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[73] Assignee: **Eastman Kodak Company,** Rochester, N.Y.

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Related U.S. Application Data

[62] Division of Ser. No. 166,897, July 28, 1971, Pat. No. 3,773,302.

[52] **U.S. Cl.** **96/100**

[51] **Int. Cl.** **G03c 1/40**

[58] **Field of Search** ..... 96/94 R, 100, 114.7

[56] **References Cited**

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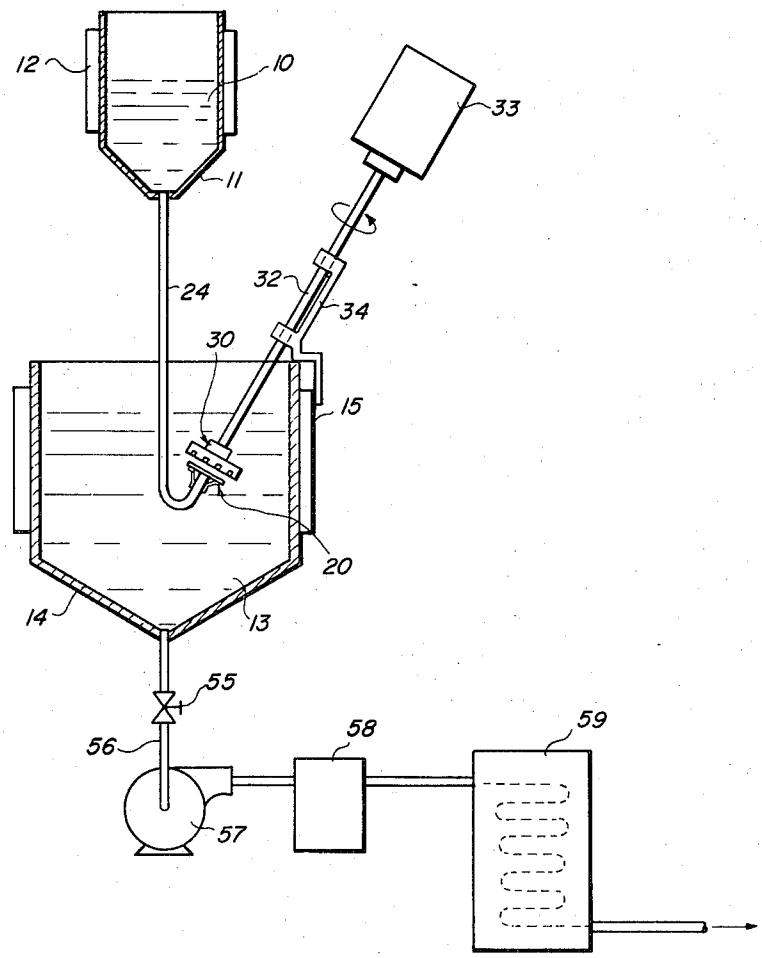
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[57] **ABSTRACT**

A method and apparatus relate to mixing solutions in which a well-stirred coupler/coupler solvent mixture is fed through a tube to an annular, flow-restriction plate arranged within an aqueous gelatin bulk mixture. A rotatable impeller is mounted in spaced relation to the plate and pumps the gelatin bulk mixture through the central opening or aperture in the plate and into the gap between the plate and the impeller. The impeller is provided with a number of concentric recesses interconnected by radial slots forming a circuitous path to the peripheral edge thereof. The flows of coupler/coupler solvent and gelatin bulk mixture are broken up by the radial slots and the annular recesses in conjunction with the fluid shear developed at the peripheral edge of the impeller.

6 Claims, 4 Drawing Figures



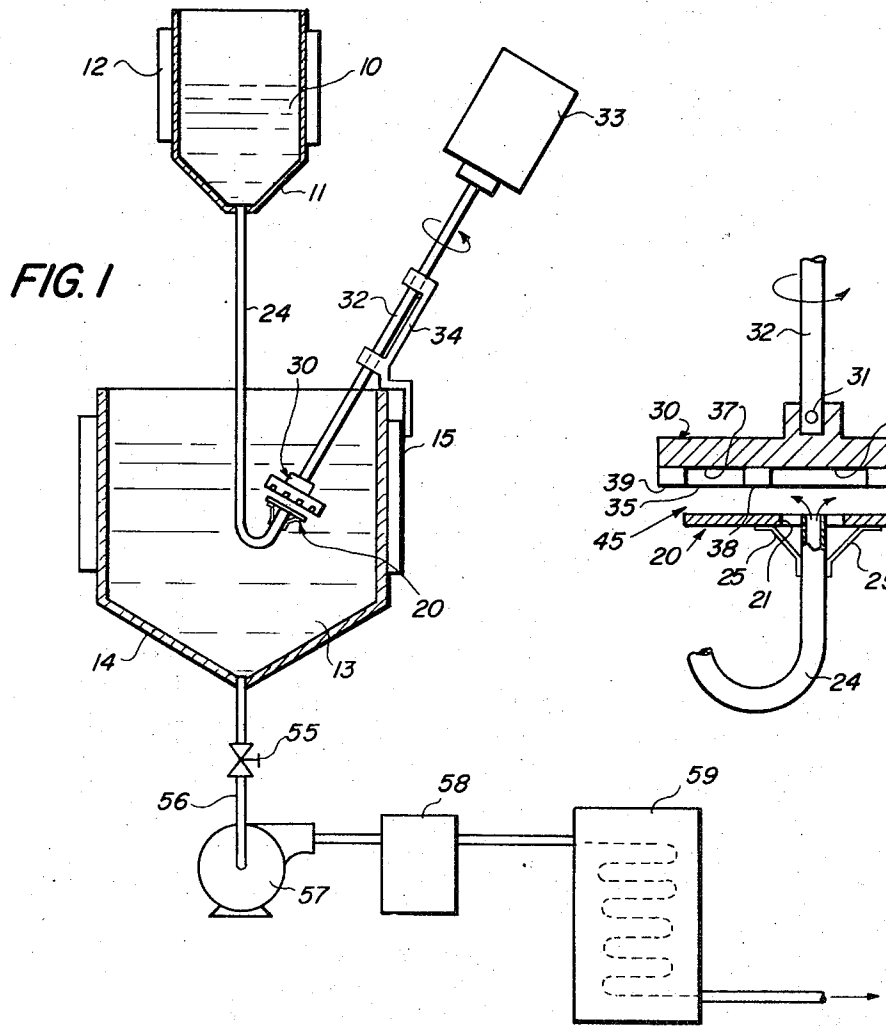


FIG. 1

FIG. 2

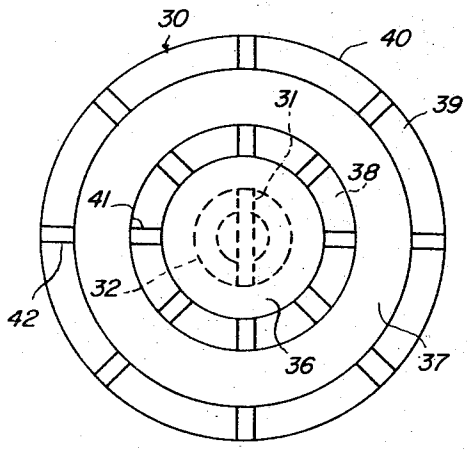


FIG. 3

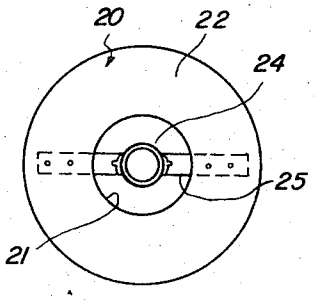


FIG. 4

PROCESS FOR MAKING COUPLER DISPERSIONS

This is a division of application Ser. No. 166,897, filed July 28, 1971, now U.S. Pat. No. 3,773,302.

FIELD OF THE INVENTION

This invention relates to a process and apparatus for the preparation of coupler dispersions and, more particularly, to a method and apparatus for preparing coupler dispersions which are crystal-free and have particle sizes of 1 micron or less.

DESCRIPTION OF THE PRIOR ART

In the photographic art the addition of respective reagents or addenda to an aqueous gelatin solution is usually accomplished by the agitation provided by a simple, propeller-type impeller. The actual dispersion is accomplished by passing the mixture, after the addenda has been added, through a colloid mill, homogenizer, or the like; and the dispersions can be stabilized by the addition of emulsifying agents, such as those of the well-known higher fatty, alcohol sulfate type.

With the addition of one or more such addenda compositions to a gelatin solution, the addition obtained results in areas of the gelatin solution having a local, high concentration of the solution which results in coagulated particles. These coagulated particles interfere with filtration of the gelatin solution and also increase the occurrence of defects in the coatings which result therefrom.

Normally, coupler dispersions for use in photographic silver halide emulsions can be prepared by mixing a coupler with a low boiling hydrophobic organic solvent, for example, ethylacetate, dispersing the mixture by passing it through a colloid mixer several times, cooling the mixture until gelled, shredding the gelled dispersion, then washing the shreds with water and drying the shreds to remove the low boiling organic solvent. At the same time, a low molecular weight, organic crystalloidal material, for example, di-n-butylphthalate, is dispersed in gelatin by passing the mixture through a colloid mill several times and filtering the dispersion through a silk screen to remove air bubbles. The two dispersions are then mixed, heated by a water bath at 40°C for several minutes, and then added to a photographic emulsion. Such a procedure is described in U.S. Pat. No. 2,801,170. A somewhat similar technique is disclosed in U.S. Pat. No. 2,801,171 for the preparation of dispersions having a low coupler to solvent ratio. In both of these patents, colloid mills are relied upon to provide a small particle size dispersion.

The prior art also discloses other means for obtaining coupler dispersions of small particle size, for example, a blender, an ultrasonic wave generator in the aqueous gelatin solution, electrostatic atomization, and more sophisticated liquid mixing apparatus which can be used for dispersing coupler/solvent mixtures in aqueous gelatin solutions. In the prior art there is no indication of the size of the coupler particles in the dispersion other than "when the two solutions are mixed using the apparatus of the present invention, the fine dispersion of color coupler is improved, since the size of the coupler particles is considerably more uniform."

As shown by the prior art, a ballasted non-hydrophilic coupler in a solvent, usually an ester, can be dissolved and dispersed mechanically by means of a homogenizer or colloid mill in gelatin in the presence of a surface-active agent. Such dispersions are then incorporated in a photographic emulsion, and a desired particle size is 1 micron or less. It is important to prevent the coupler from undergoing crystallization upon prolonged storage; and, frequently, the mixture must be passed through a homogenizer or colloid mill several times in order to obtain the desired particle size of less than 1 micron. The particle size of the coupler dispersion can effect the microscopic structure of the dye image being formed. The degree of dispersity of the dye deposit influences the absorption of the dye and the graininess and, possibly, definition of the dye image can be effected to the morphology of the dye deposit. Dyes can be formed only to the extent to which the coupler has been supplied per unit of space. Consequently, a uniform coupler dispersion having submicroscopic, that is, less than 1 micron particles would be highly desirable.

For manufacturing purposes, it would also be desirable to prepare large batches of submicroscopic uniform coupler dispersions. Obviously, blenders and other types of mixing devices do not readily lend themselves as a suitable homogenizer for such large batches of coupler dispersions. In addition, in order to obtain a coupler dispersion having the desired particle size, the dispersion must be recycled several times through a colloid mill. As a result, the use of colloid mills is very time-consuming and not particularly satisfactory for preparing a large batch of coupler dispersion.

SUMMARY OF THE INVENTION

One object of the invention is to provide a method and apparatus by which a uniform and crystal-free dispersion can be prepared.

Another object of the invention is to provide a method and apparatus by which a coupler/coupler solvent can be uniformly mixed with an aqueous gelatin solution to provide a uniform and crystal-free dispersion.

Yet another object of the invention is to provide a method and apparatus by which a uniform and crystal-free dispersion can be prepared without producing any adverse sensitometric effects relative to the final emulsion with which the dispersion is used.

A still further object of the invention is to provide a method and apparatus for preparing a coupler dispersion in which the resultant particle size in the dispersion is of the order of about 1 micron.

These and other objects and advantages of the invention will be apparent from the description which follows.

The above objects of the invention are attained by a method and apparatus in which a well-stirred coupler/coupler solvent mixture is fed through a tube to an annular, flow-restriction plate arranged within an aqueous gelatin bulk mixture. A rotatable impeller is mounted in spaced relation to the plate and pumps the gelatin bulk mixture through the central opening or aperture in the plate and into the gap between the plate and the impeller. The impeller is provided with a number of concentric recesses interconnected by radial slots forming a circuitous path to the peripheral edge thereof. The coupler/coupler solvent flows into the gap and the innermost recess and is completely surrounded by the flow of gelatin bulk mixture that is moved through the central opening by the impeller. The cen-

trifugal force generated by the impeller causes the two flows to be mixed upon movement thereof through the radial slots and the adjacent recesses to the peripheral edge of the impeller where the mixture is expelled into the gelatin bulk mixture. The flows of coupler/coupler solvent and gelatin bulk mixture are broken up by the radial slots and the annular recesses in conjunction with the fluid shear developed at the peripheral edge of the impeller.

DESCRIPTION OF THE DRAWING

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

FIG. 1 is a vertical sectional view through apparatus embodying the invention;

FIG. 2 is a vertical sectional view showing in more detail the relation of the impeller and the annular, flow-restriction plate;

FIG. 3 is an elevational view of the impeller showing the concentric impeller recesses and the radial slots interconnecting said recesses; and

FIG. 4 is an elevational view of the annular flow-restriction plate showing the central opening and the feed tube for introducing the coupler/coupler solvent liquid.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Reference is now made to FIG. 1 in which the coupler/coupler solvent liquid **10** is disclosed as being contained within a receptacle **11** that can be heated by means of a unit contained within the jacket **12** to maintain the solvent at the proper temperature. An aqueous gelatin solution **13** is contained in a tank **14**, which is provided with a jacket **15** containing heating means for maintaining the gelatin solution at the proper temperature. While the liquid **10** and solution **13** have just been described as a coupler/coupler solvent liquid and an aqueous gelatin solution, in a broader sense, the first (**10**) can be referred to as a dispersed phase liquid, whereas, the latter (**13**) can be defined as a continuous phase dispersion medium. This terminology is noted to be sure it is understood that the method and apparatus about to be described in more detail for the preparation of a coupler dispersion for use in a photographic emulsion can also be used with equivalent results for mixing any liquids that can be defined by the broader definitions.

A fixed plate member **20** is provided with an annular opening **21** and has generally planar surfaces **22** and **23**. The plate **20** is, preferably, circular in shape with a concentric, circular opening **21**, thereby providing an annular shape. A feed tube **24** is connected at one end to the receptacle **11** and is fixedly mounted within tank **14** in a manner not shown. The other end of tube **24** supports plate member **20** by means of straps **25** so tube **24** is generally central with respect to opening **21**.

A rotatable impeller member **30** is circular in shape and is secured or fixed by pin **31** to the end of a shaft **32** that is driven by motor **33**. Those elements are supported by bracket **34** mounted on tank **14** so the impeller is in the gelatin solution **13**. The impeller member **30** has a planar surface **35** and is provided with at least two concentric, annular recesses **36** and **37**. The recesses open to surface **35**, as shown in FIG. **2**, and the land **38** between recesses **36** and **37**, and the land **39** between recess **37** and the peripheral edge **40** are interconnected by a number of radial slots **41** and **42**, respectively. The impeller member **30** is immersed in the gelatin solution **13**, as shown in FIG. **1**, and is arranged with the surface **35** in close proximity to the surface **22** of plate **20**, thereby forming a gap **45** of less than 0.25 inches therebetween. By means of bracket **34** and suitable means (not shown) for mounting the tube **24**, the plate **20** and impeller member **30** are maintained in a fixed, spaced relation within tank **14** so the impeller **30** can be rotated in the gelatin solution **13**.

During operation, the impeller **30** draws the gelatin solution through opening **21**, into gap **45**, and into the innermost recess **36**. The centrifugal force generated by impeller **30** moves the gelatin solution through the radial slots **41**, into the recess **37**, and then through radial slots **42** to the peripheral edge **40**, and into the gelatin solution **13**. The impeller **30** is designed to provide a rate of about 10,000 rpm-inches (diameter × rpm). Also, the number and cross section of slots **41** and **42** are chosen so as to create a suction or vacuum at tube **24** that is at least **30** inches water.

The recesses **36** and **37** with slots **41** and **42** provide a type of circuitous path through which the liquid **10** and solution **13** are moved and mixed and finally expelled at the peripheral edge of member **30**. The circuitous path can take other forms and can be provided relative to the surface **22** of member **20** or in both of members **20** and **30**. It is believed that a more uniform and finer dispersion can be obtained if such a path is provided in both of members **20** and **30**.

With the introduction of the coupler/coupler solvent liquid, the vacuum or suction developed by impeller **30** draws the liquid into gap **45** and the innermost recesses **36**. It will be noted that with respect to FIGS. **2** and **4**, that the flow of gelatin solution through opening **21** completely surrounds the flow of the coupler/coupler solvent liquid via tube **24**. As the two flows of liquid enter recess **36**, they are broken up and thoroughly intermixed by the radial slots **41** and **42**, the annular recesses **36** and **37**, and the fluid shear produced at the peripheral edge **40** of the impeller **30**. With this action, the two flows are thoroughly mixed before being introduced into the gelatin bulk mixture **13** by the movement thereof through slots **41** and **42** and gap **45**.

After a complete dispersion has been accomplished, a valve **55** in a line **56** is opened connecting tank **14** to a pump **57** which moves the dispersion through a filter **58** and then into and through a heat exchanger **59**. Upon discharge from the heat exchanger **59**, the dispersion can be treated and converted into a firm jelly or solid form for storage purposes.

The following example will serve to illustrate the invention, but is not to be considered as a limitation thereof.

The coupler/coupler solvent mixture and aqueous gelatin solution are made as follows:

Coupler/coupler solvent mixture

N-(p-Benzoylacetamidobenzenesulfonyl)-N,γ-Phenylpropyl-p-toluidine	4 Kg.
tri-cresyl phosphates	2 Kg.
2-ethoxy ethylacetate	8 Kg.
Temperature	137.8°C

Aqueous gelatin mixture

Gelatin	2.994 Kg.
Distilled water	26.943 Kg.
Sodium Alkylnaphthalene sulfonate (NEKAL BX-78, GAF Corporation)	2.994 Kg

The coupler/coupler solvent mixture is dissolved with stirring at 137.8°C, filtered and then added (over a period of 5 min.) to the aqueous gelatin solution using the process and apparatus described above.

The resulting dispersion is removed from the tank, passed through a centrifugal pump, filtered and chilled to 10°C to set the dispersion. If desired, the dispersion can be washed as described in Fierke et al., U.S. Pat. No. 2,801,171. In the case where volatile solvents are used, the volatile solvent can be removed by evaporation.

This technique permits a uniform and crystal-free dispersion to be prepared. The resultant particle size is of the order of one-half to one micron. For a still further reduction in particle size, the dispersion can be passed through a colloid mill instead of a centrifugal pump prior to the filtration step.

This 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. A method of preparing a generally uniform and crystal-free coupler dispersion having a particle size of 1 micron or less which comprises the steps of:

introducing a flow of coupler/coupler solvent solution into an open-end gap formed by the facing surfaces of a rotatable plate member and a fixed member having a central opening and arranged in an aqueous gelatin solution, the facing surface of at least one of said members being provided with recesses forming a circuitous path from the center to the peripheral edge thereof; and

maintaining a flow of said aqueous gelatin solution through said opening;

whereby the flows of said coupler/coupler solvent solution and of said aqueous gelatin solution are thoroughly mixed during movement through said gap and said path to the open-end of said gap for expulsion into said aqueous gelatin solution.

2. The method in accordance with claim 1 wherein said flows are mixed centrifugally and expelled from the open end of said gap as a continuous flow into said aqueous gelatin solution.

3. The method in accordance with claim 1 wherein the flow of said coupler/coupler solvent solution is introduced generally centrally of the flow of said aqueous gelatin solution through said opening.

4. The method in accordance with claim 1 wherein the flow of said coupler/coupler solvent solution is maintained by the vacuum created in said gap by said rotatable plate member.

5. The method in accordance with claim 1 wherein the flow of said aqueous gelatin solution into said gap surrounds the flow of said coupler/coupler solvent solution.

6. The method in accordance with claim 4 wherein the created vacuum is at least 30 inches water.

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