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METHOD FOR DISPERSING NON-AQUEOUS SOLUTION IN AQUEOUS GELATIN SOLUTIONS USING AN ASPIRATING AGITATOR

Filed March 30, 1964

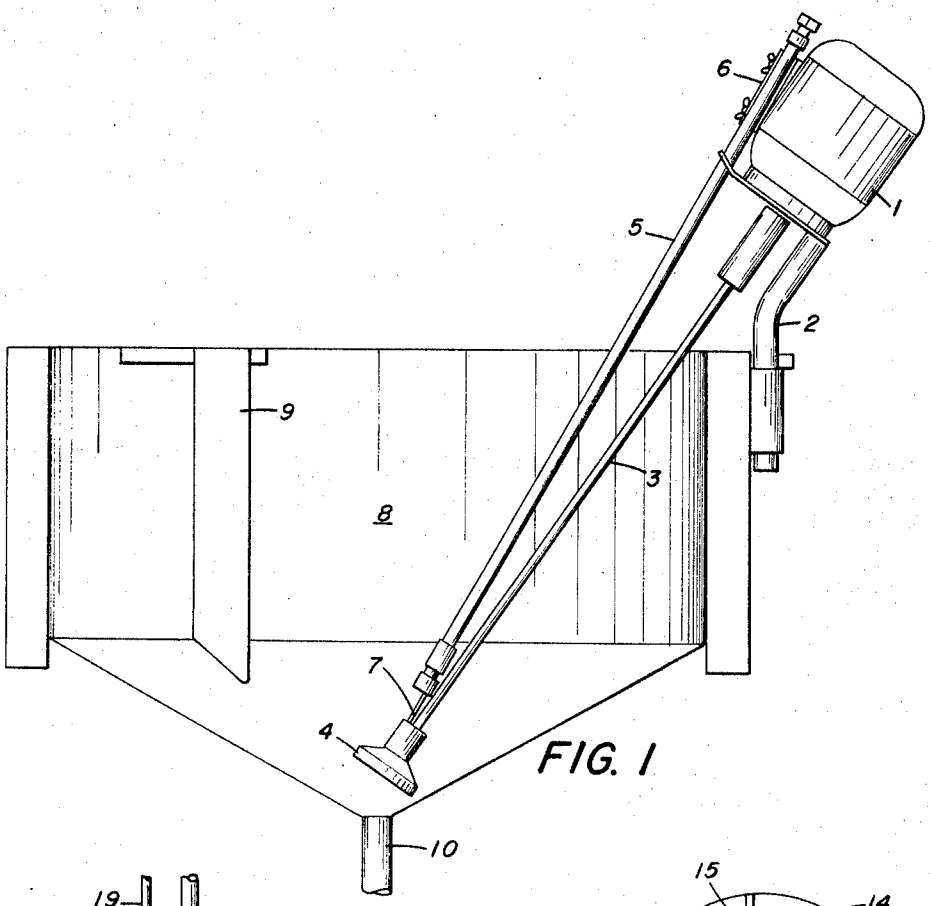

FIG. 1

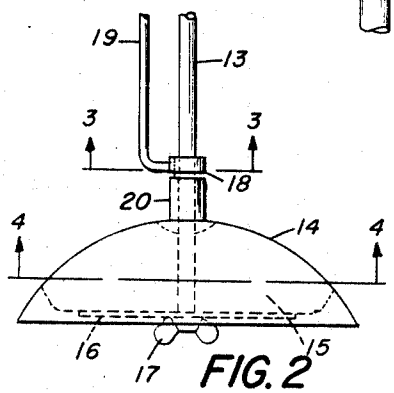

FIG. 2

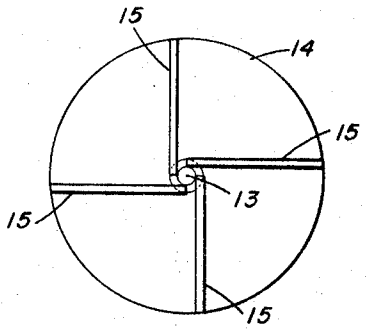

FIG. 4

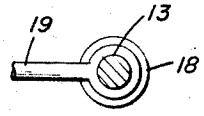

FIG. 3

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METHOD FOR DISPERSING NON-AQUEOUS SOLUTION IN AQUEOUS GELATIN SOLUTIONS USING AN ASPIRATING AGITATOR

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Int. Cl. B01f 7/02; G03c 11/00

ABSTRACT OF THE DISCLOSURE

For dispersing liquid addenda in aqueous gelatin emulsions, e.g. in photographic emulsions, local dehydration of gelatin by the addenda is avoided by introducing such addenda below liquid surface as the emulsion is rapidly agitated. Aspirator mixing device draws addenda into emulsion with suction induced by a mixing propeller.

This invention relates to a method of dispersing water-miscible liquids in hydrophilic colloid solutions and an apparatus useful for this purpose.

In the making of gelatin compositions for use in photographic manufacture and especially photographic emulsions it is frequently desirable to introduce chemicals therein which must be dissolved in water-miscible non-aqueous solvents, before they are incorporated in the aqueous gelatin solutions. Some materials which are often introduced into photographic gelatin coating solutions or photographic emulsions are dyes, sensitizers, hardeners, antifoggants, stabilizers, etc. Often compounds of this nature which are most effective are preferably introduced into the gelatin compositions in the form of their solutions in non-aqueous organic solvents. The introduction of such solvents into gelatin compositions often cause local dehydration of the gelatin resulting in particulate matter which cannot be readily redispersed in the gelatin composition. Such particulate matter may subsequently cause defects in film prepared using these photographic gelatin compositions.

Various procedures have been suggested for minimizing the dehydration of gelatin as for example by adding the non-aqueous solvent solution very slowly to the surface of the gelatin composition while the bulk of that composition is being agitated by a rotating impeller within a vessel. Various nozzles and spreading devices have been considered for use in dispensing the solvent before it contacts the surface of the batch. Foam on the surface of such compositions if contacted by such solvents is particularly susceptible to dehydration due to the unfavorable solvent concentrations therein. None of the previous proposed methods have been sufficiently effective in minimizing product degradation from visible defects in the product from insoluble particles. Filtering the final solution is inadequate for eliminating those defects.

One object of our invention is to provide a method of incorporating non-aqueous solutions into aqueous-gelatin compositions avoiding dehydration of the gelatin contained in the bulk solution. Another object of our invention is to provide a method of incorporating non-aqueous solutions into aqueous gelatin compositions which avoids contact with the surface foam of the gelatin composition, foam being especially sensitive to dehydration. A further object of our invention is to provide a method of mixing non-aqueous solutions and aqueous gelatin compositions eliminating manual lifting and pouring from containers.

A still further object of our invention is to provide an apparatus which is useful in embodying the procedure for incorporating non-aqueous solvent solutions into aqueous gelatin compositions in the manner described herein. Other objects of our invention will appear herein.

In accordance with our invention non-aqueous solutions are incorporated into aqueous gelatin compositions by aspirating the non-aqueous solutions from an external container into a batch consisting of an aqueous solution as it is rapidly dispersed and mixed by means of a rotating propeller encased in a shell to form a confined area of differential pressure. The rapidity of mixing at the point of entry of the non-aqueous solution prevents local concentrations causing dehydration of the gelatin so that few, if any, insoluble particles are created. Our invention involves the circulation of an aqueous gelatin composition into a highly agitated confined area into which a small stream of non-aqueous solution is being fed which is then dissipated into the bulk gelatin solution by means of an annular discharge space.

The procedure in accordance with our invention may more readily be described by referring to the novel apparatus in which the introduction of the non-aqueous solvent solution into the aqueous gelatin composition is carried out.

In the accompanying drawings FIG. 1 illustrates, in section, apparatus in accordance with the invention in use in a container for the bulk gelatin solution.

FIG. 2 is a drawing in section of an impeller in accordance with the invention in which the shell of the impeller rotates.

FIG. 3 is a view in section taken through line 3—3 of FIG. 2 showing the structure of the collar employed in FIG. 2.

FIG. 4 is an illustration in section taken through 4—4 of FIG. 2 showing the arrangement of the impeller blades within the aspirating agitator of FIG. 2.

In FIG. 1 a driving means for the impeller, in this case an electric motor **1**, is attached to the vessel **8**, which contains the gelatin solution, by means of a tubular support and bracket **2**. Shaft **3** which is an extension of the axis of motor **1** is attached to agitator blades within shell **4** to which the agitator blades are attached whereby the shell rotates upon rotation of the blades by shaft **3**. Also fastened to driving means **1**, is a hollow support tube **5** attached to the motor by means of clamps (or some other type of fixture) **6**. At the other end of the support tube **5** is nozzle **7** so positioned that liquid passing through tube **5** is introduced into the space confined by shell **4**. The rotation of the impellers creates movement of the liquid contained in the vessel **8** whereby the liquid enters the shell **4** in the narrow neck portion thereof and exits through an effluent annulus on the bottom of shell **4**. Vessel **8** may desirably be provided with a baffle **9** which can be varied in size and placed in a variety of positions in the vessel. Vessel **8** is also provided with an outlet **10** whereby the contents of the vessel **8** may be removed when and if desired.

FIG. 2 shows in detail one design of an aspirating agitator useful in incorporating non-aqueous solvent solutions into aqueous gelatin solutions in accordance with the invention. In FIG. 2 the unit composed of blades **15** is held on shaft **13** by wingnut **17** so that rotation of shaft **13** causes rotation of the blades or paddles. In FIG. 2 the blades are joined to shell **14** whereby the blades and the shell rotate together. Held on the end of the shaft by wingnut **17** is a disk **16** restricting the bottom of the shell to an effluent annulus.

For introduction of non-aqueous solvent solution a collar **18** is provided into which an inlet **19** leads. The details of the collar are more clearly illustrated in FIG. 3 which shows the inlet **19** which leads into the space between collar **18** and the shaft **13** where the non-aqueous solvent solution comes in contact with the aqueous gelatin solution flowing through sleeve **20** into the confined area within shell **14** in which agitation occurs.

The set up of apparatus within the shell is more clearly illustrated by FIG. 4 which shows the arrangement whereby the rotatable blades **15**, are affixed on the shaft and the attachment of the blades, **15**, to the shell **14**. Instead of the shell rotating with the blades, modification of our invention involves the blades being not attached to the shell which is held stationary such as by being attached to one or more supports such as tube **5** in FIG. 1 or collar **18** as shown in FIG. 2. If it is considered desirable to introduce more than one non-aqueous solvent solution to the aqueous gelatin composition this can be done by providing more than one inlet to the collar if a set up such as illustrated in FIG. 2 is used or more than one suction tube may empty into the inlet sleeve of shell **4** if the arrangement is as illustrated in FIG. 1.

The process in accordance with our invention is carried out by introducing the non-aqueous solvent solution into the inlet sleeve of the shell of the agitator submerged below the surface of the aqueous gelatin solution. Incorporation of the non-aqueous material into the gelatin solution is preferably accompanied by rotating the agitator at speeds between 400 and 3600 r.p.m. and preferably between 750 and 2000 r.p.m. Flow rates of the addenda solution may be varied over a wide range e.g. 0.1–50 ounces per sec. with satisfactory results. Ordinarily the gelatin solutions to which the non-aqueous solvent solutions are added have a gelatin content of 1–20% although here again the concentration of the gelatin solution is a matter of selection for the individual operator. The flow rates of the gelatin composition can be varied by changing the impeller design, the annular effluent area, the annular inlet area or the speed of rotation or a combination of any of these.

The following non-limiting examples illustrate the use of the invention for incorporating a non-aqueous solvent solution into a gelatin-containing silver halide photographic emulsion.

Example 1

A silver bromoiodide gelatin photographic emulsion was prepared for use as the green-sensitive layer of a multi-layer color film product. The initial batch of about 140 pounds contained approximately 5% gelatin in water and was heated in a vessel to a temperature of 120° F. A methanol solution of sensitizing dyes was added at the rate of about 4–5 pounds per minute to the photographic emulsion in an amount of 60 cc. per pound of emulsion, using the aspirating agitator illustrated by FIG. 2 of the drawings and under the following conditions:

Agitator (diameter at 1750 r.p.m.) ——inches—	5⅛
Addenda feed line (tubing) ——————do——	¼
Effluent annulus (width) ——————do——	⅛
Available suction ——————inches of mercury—	20

Also added was a solution of anti-foggant in acetone added at the same rate. The emulsion was filtered and coated. The defect index of the composition was 1 as compared to a defect index of 5 where the same materials are added to photographic emulsion by adding to the surface of the emulsion while being stirred.

The following example illustrates the advantages obtained when the aspirating agitator is used for the addition of an aqueous of an acid to a silver halide gelatin emulsion.

Example 2

A silver bromoiodide gelatin was prepared as described in Example 1. An aqueous solution of 2.5 N sulfuric acid was added at the rate of about 1 ounce per second to the emulsion in an amount of about 10 cc. per pound of emulsion using the aspirating agitator described in Example 1. The emulsion was filtered and coated as described in Example 1. The defect index of the coating was considerably lower than the defect index of a similar coating made from an emulsion where the acid solution was added to the photographic emulsion by the conventional procedure wherein the acid solution is added to the surface of the emulsion while the emulsion is being stirred.

In the photographic art it is frequently necessary to add various types of solutions to aqueous hydrophilic colloid solutions especially to silver halide photographic emulsions which contain a hydrophilic colloid as a carrier for the silver halide crystals. For instance, sensitizing dyes and antifoggants are commonly added in the form of their solutions in organic solvents. The solvents are prone to cause formation of coagulated particles in the hydrophilic colloid solution. Aqueous solutions of hardeners are commonly added to the hydrophilic colloid solutions. Temporary high concentrations of hardeners may cause over-hardening of a portion of the hydrophilic colloid to produce insoluble particles. It is often desirable to add acid to hydrophilic colloid solutions particularly photographic emulsions to impart a desired pH. Frequently such hydrophilic colloid solutions contain gelatin derivatives or other polymeric vehicles which are sensitive to an acid pH; hence, unless care is used in the addition of the acid or alkali to the colloid solution, some precipitation of the colloid may occur.

Samples of hydrophilic colloids which may be used alone or in mixtures with gelatin are:

(1) Cellulose ether esters of the type described in Kodak U.S. Patent 2,725,293, e.g. cellulose ether phthalate.

(2) Carboxymethyl proteins of the type described in Kodak U.S. Patent 3,011,890.

(3) Dibasic acid derivatives of gelatin as described in Kodak U.S. Patent 2,614,928.

(4) Polyvinyl pyrrolidones of the type described in British Patent 867,899.

(5) Polyacrylamides of the type described in U.S. Patent 2,533,166.

(6) Acrylate-acrylic acid copolymers of the type described in U.S. Patent 3,062,674.

(7) Carboxyhydroxyethyl cellulose of the type described in Kodak U.S. Patent 3,003,878.

(8) Carboxylated polyvinyl acetals of the type described in Kodak U.S. Patent 3,003,879.

(9) Dibasic acid esters of polyvinyl alcohol as described in Kodak U.S. Patent 3,000,741.

(10) Polyvinyl alcohol.

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

We claim:

1. A method of mixing liquid addenda into a body of aqueous hydrophilic colloid solution comprising, (1) circulating hydrophilic colloid solution of said body through a confined space defined within said body by an axial shell having a solution intake opening at the axis of said shell communicating from said outer surrounding solution to said confined space and having a solution outlet opening at the periphery of said shell communicating from said confined space to the said outer surrounding solution, by means of an impeller rotating in said confined space with force sufficient to drive liquid through said confined space from said axial intake openings to said peripheral outlet opening and, (2) simultaneously aspirating liquid addenda into said confined space through said axial intake opening from tubes means communicating from a

liquid source outside said body of solution to said solution intake opening.

2. A method defined by claim 1 wherein said liquid addenda is a non-aqueous addenda for said gelatin solution.

3. The method defined by claim 1 wherein said hydrophilic colloid solution is a hydrophilic colloid-silver halide photographic emulsion.

4. The method defined by claim 3 wherein said liquid addenda is a non-aqueous liquid addenda for a photographic silver halide emulsion.

5. The method defined by claim 3 wherein said hydrophilic colloid is gelatin.

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J. TRAVIS BROWN, *Primary Examiner.*

U.S. Cl. X.R.

259—23

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,425,835 February 4, 1969

Benjamin A. Johnson et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 71, after "aqueous" insert -- solution --. Column 4, line 75, "tubes" should read -- tube --.

Signed and sealed this 24th day of March 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents