Aug. 6, 1968 J. C. McFALL ET AL 3,396,027

METHOD OF NOODLING GELATIN DISPERSIONS

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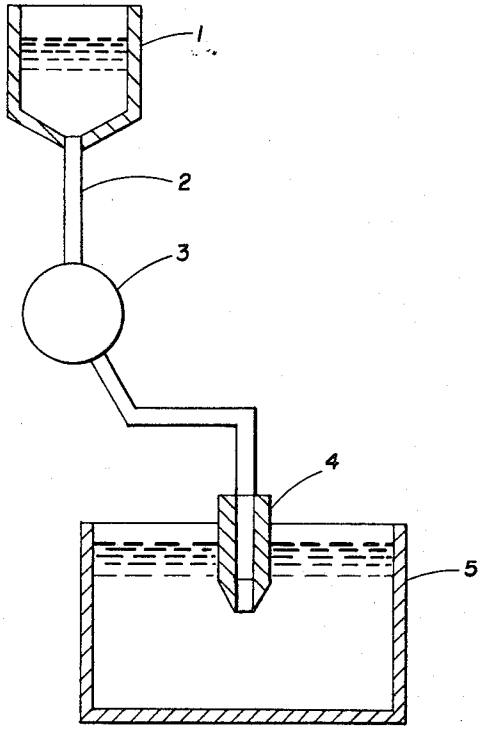
FIG. 1



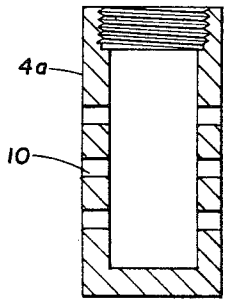


FIG. 2

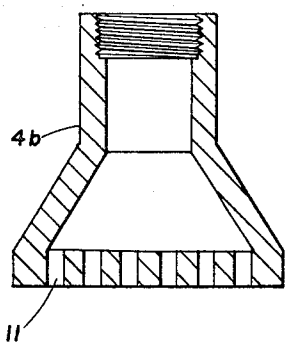


FIG. 3

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METHOD OF NOODLING GELATIN DISPERSIONS

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ABSTRACT OF THE DISCLOSURE

A process for forming noodles of photographic gelatin includes passing an aqueous gelatin dispersion through an extrusion head, the orifices of which are immersed in chilled water.

This invention relates to the simultaneous setting and subdividing of aqueous gelable hydrophilic colloid compositions, and particularly to a method and apparatus for rapidly chill setting liquid photographic gelatin dispersions in a form with a high surface-to-volume ratio to facilitate washing.

In making photographic silver halide gelatin emulsions and in the preparation of gelatin dispersions of color-forming couplers, often unwanted water-soluble by-products, auxiliary solvents, etc. remain, whose removal is desirable. A usual procedure for removing the unwanted materials involves jelling the dispersion by chilling, subdividing the gelled mass into shreds or noodles, and washing the noodles with cold water. This involves separate setting and noodling operations and requires considerable space for chill tanks to contain the dispersions so that they can be noodled prior to washing. To obviate successive separate batch operations of setting the dispersions, shredding or noodling, and transferring to a washing tank, Craft U.S. Patent 2,316,845 issued Apr. 20, 1943, proposed a continuous mechanized procedure comprising pumping melted gelatin dispersion into a heat exchanger to set it to a gel, which is forced through a perforated plate to subdivide it into noodles which are delivered to a washing unit. This procedure uses high pressures to force the jelled dispersion through the noodling head.

We have found that the separate operations of chill setting and noodling can be combined and the high pressure ordinarily used in noodling may be eliminated by employing a device and process whereby the liquid is set directly in the form of well-defined noodles, which have sufficient cohesion to prevent loss of colloid by solution in wash water and of small enough diameter to facilitate rapid washing.

One object of our invention is to obviate setting tanks, heat exchangers, and refrigerated storage rooms in handling gelatinous coupler dispersions or photographic gelatin-silver halide emulsions prior to washing.

Another object of our invention is to avoid the high pressures normally used in noodling colloid gels.

A further object of our invention is to provide a unique method for decreasing the tendency of color-forming couplers to crystallize when incorporated in a dispersion.

We have accomplished these objects by passing liquid aqueous gelatin dispersions or emulsions directly from the last stage of the mixing operation, colloid mill or homogenizer used in their preparation through the tiny orifices of a glass, plastic, or other rigid heat insulating diaphragm into chilled water in a washing tank.

The orifices in the extrusion head should advantageously be between about 0.015 inch (minimum diameter to insure that the extruded noodles have sufficient body to withstand vigorous washing) and about 0.125 inch (maximum diameter to insure that the noodles harden or set up immediately on leaving the extrusion head) to avoid losing some of the dispersion as "fines" and to avoid adhesion

between separate noodles. Washing takes longer with increase of the average diameter of the noodles. It requires about four times as long to wash a noodle extruded through a 0.10 inch opening as one extruded through a 0.03 inch opening at same pressure.

The perforated extrusion diaphragm or head should provide adequate heat insulation of the walls of the extrusion orifices to prevent the dispersion or emulsion from setting up in the orifices. The head may be made from glass, polystyrene, Synthane, Boltaron, or other plastic. Metal can be used in the construction of the head providing the walls of the extrusion channels and the surfaces in contact with the melted dispersions and the cold water are adequately insulated whereby heat transfer is retarded.

Photographic silver halide emulsions are typically prepared by mixing a solution of alkali halide, such as potassium bromide and a solution of silver nitrate in the presence of gelatin. The resulting dispersion may be jelled by chilling, which jelled mass is subdivided or noodled and washed in cold water to form a "washed emulsion."

In the widely used "solvent dispersion" technique for suspending color-forming couplers in gelatin, the coupler may be dissolved in a mixture of a high-boiling water-immiscible solvent and a water-soluble auxiliary solvent or alternatively in a solvent of low water solubility. This solution may be emulsified in a melted aqueous gelatin solution, and the resulting dispersion may be chilled to form a gel, shredded, and washed to remove the auxiliary solvent.

Typical ratios of coupler solvent to coupler are for example from about 2 to 1 up to about 3 to 1, as illustrated in the examples of Jelley U.S. Patent 2,322,027, issued June 15, 1943; Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957; Julian U.S. Patent 2,949,360, issued Aug. 16, 1960; and Vittum U.S. Patent 2,801,170, issued July 30, 1957.

The ratio of coupler solvent-to-coupler is normally kept sufficiently high to avoid crystallization by the coupler in the solvent. When the dispersion is jelled slowly, e.g., by the prior art procedures of chill setting, some couplers crystallize to some extent even at the maximum solvent levels which can be tolerated in emulsion coating. Our invention obviates this problem by enabling the dispersions to be set and washed quickly so that crystallization of the couplers is prevented.

The accompanying drawings illustrate apparatus useful in the invention. FIGURE I is a plan view of a combination of apparatus in which the procedure described herein can be conveniently carried out provided with a container, **1**, having therein the dispersion to be refined, connected by a conduit or pipe **2** with the extrusion head **4**. Preferably present in this line is a metering system **3** to control flow and to supply pressure additional to that supplied by gravity. The extrusion head, **4**, is preferably composed of some material which is a poor heat conductor to avoid cooling of the dispersion while in the orifice. Vessel, **5**, into which the material is extruded contains chilled water such as at about 40° F. the level of which water contacts the extrusion head.

FIGURES II and III are plan views of modified types of extrusion heads which may be used, the outlets of the orifices of which when used being immersed in the chilled water to assure immediate formation of noodles. The orifices of the various extrusion heads should have diameters within the range of 0.015–0.126 inch.

The temperature of the gelatin dispersion to be extruded should be between about 75 and 90° F. depending on the percent gelatin in the mixture. The preferred temperature of the wash water should be between about 36 and 50° F. optimally about 40° F.

Chilled wash water is passed continuously through the region around the extrusion head either concurrent or

countercurrent to the noodles as they are being formed, to prevent local heating that would interfere with the setting of the noodles.

The orifices in the extrusion head must have a diameter between about 0.015 and 0.125 inch in diameter with a preferred diameter of about 0.065 inch. Pumping pressure of the emulsion or dispersion through the noodling head is advantageously between about 1 to 10 pounds per square inch and is adjusted to minimize loss of gelatin which might result from extruding the noodles too rapidly.

The various extrusion heads are merely illustrative and the invention is not limited to these particular types.

Our invention is further illustrated by the following examples which do not restrict the invention.

Example I

A gelatin-silver chloride emulsion containing 0.45 lb. of gelatin per mole of silver halide and having a total weight of 8.1 lb. per mole of silver halide was extruded through a polystyrene extrusion head made from 1.0 inch rod having a center opening of 0.5 inch and twelve 0.055-inch-diameter orifices off of the center opening submerged in flowing cold distilled water (about 40° F.). The noodles formed were firm and held together through the washing cycle. The noodles after washing were placed in distilled water and and was warmed to 80° F. forming a liquid emulsion composition. The emulsion thus obtained was provided with sensitizers and other desired addends and was coated out onto a support to form photographic products.

Example II

Five hundred pounds of silver chlorobromide emulsion containing 50 pounds of cattle hide gelatin and 50 moles of silver halide was extruded through a Synthane extrusion head heaving 120, 0.312 inch diameter orifices into cold water. The walls of the extrusion head were one-fourth of an inch thick. The emulsion jelled immediately when it came in contact with the cold wash water. The noodles were firm and held together throughout the washing cycle. An emulsion coating prepared using this dispersion after conventional finishing treatment gave a silver image of excellent quality after image exposure and conventional processing.

Example III

One hundred grams of an oil-soluble yellow coupler were dissolved in 200 grams of 2-(2-butoxyethoxy)ethyl acetate at 220° F. This solution was dispersed in a mixture of 795 grams of a 10% gelatin solution, 36 cc. of 10% aqueous alkanol B solution and 200 cc. of water at 138° F. and then passed three times through a colloid mill. It was then cooled to 89° F. and pumped through a single orifice extrusion head made of a one-inch glass rod having an opening of 0.050 inch diameter, into cold wash water to form noodles and washed. The noodles were firm. A small quantity of the washed dispersion was remelted and examined under a microscope. The dispersion showed no sign of crystallization. Attempts to make this dispersion by other techniques without formation of crystals of detrimental size were unsuccessful. An incorporated-coupler photographic color emulsion prepared with this dispersion yielded an excellent yellow photographic dye image after image exposure and conventional color processing.

Example IV

One thousand grams of any UV absorber selected from those listed in German Patent No. 1,166,623 of Sawdey and 68 grams of 2,5-di-n-octylhydroquinone were dissolved in 500 grams of 2-(2-butoxyethoxy)ethyl acetate at 266° F. and dispersed in a solution containing 5600 grams of 10% gelatin, 370 cc. of 10% aqueous alkanol B solution and 1670 cc. of additional water at 140° F. This mixture was then homogenized three times through a colloid mill and cooled to 89° F. It was then pumped through an extrusion head having walls made of ⅜ in. thick Boltaron (solid polyvinyl chloride) containing fifty 0.050 in. diameter orifices, into 36° F. water to form noodles. The noodles were washed in a tank of flowing cold water. The noodles were firm and did not break up during the washing cycle.

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 with the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A method for the instantaneous noodling of an aqueous gelatin dispersion which comprises passing said dispersion under pressure through at least one orifice, having a diameter of 0.125 and 0.015 inch contained in a heat insulating extrusion head, at least the orifice being immersed in water having a temperature within the range of 36–50° F.

2. The process of claim 1 wherein the aqueous gelatin dispersion contains a suspension of color forming coupler.

3. A method for the instantaneous noodling of an aqueous gelatin dispersion which comprises passing said dispersion under pressure through a heat insulating extrusion head, which has at least one orifice between about 0.125 and 0.015 inch in diameter, at least the orifice being immersed in water having a temperature on the order of 40° F.

4. A method for the instantaneous noodling of a photographic gelatin-silver halide emulsion which comprises passing said emulsion in liquid form under pressure into a heat insulating extrusion head, provided with an orifice between about 0.125 and 0.015 inch in diameter, and extruding said photographic emulsion immediately into water having a temperature on the order of 40° F., while at least the orifice of said head is immersed in the water.

5. A method of preparing washed gelatin-silver halide photographic emulsions which comprises passing a gelatin-silver halide photographic emulsion in liquid form through a heat insulating extrusion head, provided with an orifice having a diameter of 0.015–0.125 inch, immediately into water having a temperature on the order of 40° F. while at least the orifice of said head is immersed in the water thereby forming noodles of the photographic emulsion, separating the noodles from the chilled water, washing said noodles with further chilled water and then mixing the noodles with mineral free water and supplying a temperature whereby melting of the noodles occurs and a flowable photographic emulsion composition is obtained.

References Cited

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J. TRAVIS BROWN, *Primary Examiner.*