Purification and concentration of silver halide emulsions

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The Book Barn, Westbourne, Hants. PO10 8RS. UK
Tel: +44 (0)1243-377977 Fax: +44 (0)1243-379136
e-mail : info@ResearchDisclosure.com

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In the formation of silver halides by precipitation, in the presence of a peptizer, from a water soluble silver salt solution such as, for example silver nitrate, and Group I halide solution, soluble salts, generally nitrates, are also produced.

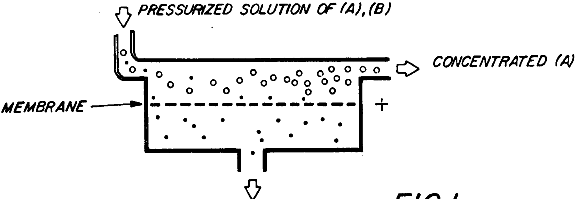
PRESSURIZED SOLUTION OF (A), (B)
CONCENTRATED (A)
MEMBRANE
+
SOLUTION OF (B)

FIG I

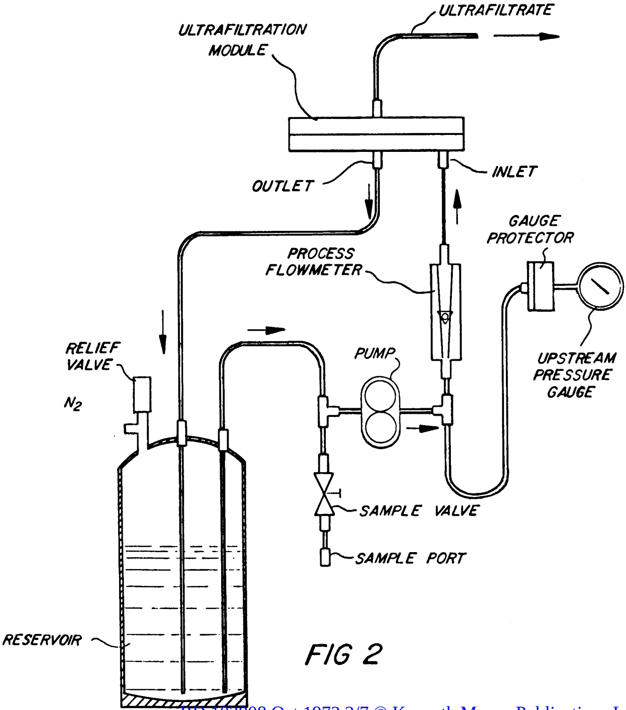
ULTRAFILTRATE
ULTRAFILTRATION MODULE
OUTLET
INLET
GAUGE PROTECTOR
PROCESS FLOWMETER
UPSTREAM PRESSURE GAUGE
PUMP
RELIEF VALVE
N_2
SAMPLE VALVE
SAMPLE PORT
RESERVOIR

FIG 2

In order to obtain high quality photographic products, it is generally necessary to remove the soluble salts from the emulsion.

Improved photographic processes comprising washing and/or concentrating silver halide emulsions can now be provided which comprise removing extraneous soluble salts by passing the peptized silver halide precipitate or emulsion, under pressure, through an ultrafiltration module such that the extraneous salts pass through a semipermeable membrane and a retentate is obtained comprising silver halide precipitated in the presence of a peptizer.

One preferred embodiment relates to the preparation of photographic silver halides. The process comprises precipitating from a solvent, in the presence of a peptizer, a silver halide from a soluble silver salt and a soluble halide salt, and removing extraneous soluble salts by passing the mixture of solvent, silver halide precipitated in a peptizer and extraneous soluble salts through an ultrafiltration module. The filtrate obtained comprises solvent and soluble silver salts whereas the retentate comprises silver halide precipitated in a peptizer, solvent and a substantially reduced concentration of extraneous soluble salts.

Ultrafiltration or membrane ultrafiltration is the technique of selectively separating low molecular weight materials from higher molecular weight materials such as polymers dissolved or suspended in the same solvent. The selective separation is effected by hydraulically pressuring a solution against a synthetic semi-permeable membrane which is constructed so as to selectively pass all molecules below a particular size and retain the larger molecules.

As shown in Figure 1, a pressurized solution of solvent, silver halide precipitated in the presence of a peptizer (A) and extraneous soluble salts (B) is fed into the ultrafiltration module through an input feed line and passed over a semi-permeable membrane over which a pressure differential is maintained. A solution of extraneous salts (B) passes through the membrane while the remaining solution (A) is retained by the membrane and passes out of the module through an output orifice.

Figure 2 is a schematic representation of the general system for preparing silver halides including the ultrafiltration module of Figure 1. The precipitated silver halide in a peptizer solvent and extraneous salts are supplied to the reservoir by well known means. The solution is then pumped through a process flowmeter into the ultrafiltration module of Figure 1. The extraneous salts are extracted as the ultrafiltrate whereas the retentate is passed back into the reservoir in a recycle operating mode. In the alternative, a number of ultrafiltration modules may be connected in series such that the retentate from the proceding module is fed into the input line of the succeeding module. Prior to the successive passing of the solution through the modules the solution can be rediluted with solvent for washing purposes or in the alternative the solution need not be rediluted for purposes of concentration.

The membranes employed in ultrafiltration modules are typically "anisotropic membranes" which comprise a very thin layer of extremely fine pore texture supported upon a thicker porous structure. The significant properties of these membranes are their high hydraulic permeability coupled with the ability to block the passage of certain solute molecules without readily becoming clogged by the retentate. The size and shape of the molecules to be retained will determine the pore size of the membrane or preferably the molecular weight cut off of the membrane. The membranes will generally have a molecular weight cut off from about 500 to about 300,000, preferably about 500 to about 50,000. However, molecular weight cut off can be readily varied outside the preferred range. It is readily understood that the molecular weight cut off should generally not be greater than the molecular weight of the peptizer.

The input pressure maintained over the membrane can vary over a wide range. Typically the input pressure is about 100 psi and the outlet pressure is up to about 10 psi. The trans-membrane pressure can be from about 40 to about 60 psi. These pressures, however, can vary above and below these figures and are limited only by such factors as the capabilities of the pumping equipment, the viscosity and concentration of the retentate, the degree of purity desired for the retentate, the desired flow rate and other factors which would be well known in the art.

The silver halide emulsions prepared in accordance with this invention can be made by any of the precipitation and ripening procedures employed fpr making silver halide grains.

Silver halide crystals freshly precipitated in the presence of a peptizer can be washed or purified by passing a solution of the freshly precipitated silver halide through an utrafiltration module. The washing or passage through an ultrafiltration module is continued until the silver halide emulsions are substantially free of soluble extraneous ions such as, for example, nitrate ions or soluble halide ions. Typically, therefore, the silver halide solution is passed through an ultrafiltration module a plurality of times, the number of times being dependent on such factors as the soluble salt concentrations obtained during precipitation, the melt weight, the silver halide to peptizer ratio, etc. It is generally the practice to wash the silver halide emulsions until the pAg has been lowered to about 8. It has generally been found that the soluble salt content decreases in accordance with a mass balance from one cycle to the next. For example, should an emulsion be concentrated to one fourth of its initial volume then rediluted with distilled water, the conductivity measurements would reflect that 75% of the soluble salts have been removed. With a second cycle 93.75% of the soluble salts are removed and with a third cycle 98.4% of the soluble salts will have been removed.

The ultrafiltration technique is not affected by the soluble salt concentration. For higher salt concentrations, additional wash cycles may be required.

For maximum filtrate flux, it is desirable to have the peptizer concentration at a minimum. It is also desirable to maintain a high shear rate at the membrane surface to minimize build up of rejected silver halide and peptizer. The average washing rate (in terms of silver moles washed per hour) for a silver halide emulsion having a high silver halide concentration will be greater than for a silver halide emulsion having a low silver halide concentration. The filtrate removal rate, however, will be about the same for either emulsion at a given peptizer concentration and about the same time will be required to complete a wash cycle.

In the process of washing the silver halide emulsions, the retentate can be recycled continuously through the single module or, as described earlier, two or more modules can be connected in series with the retentate of the preceding module being fed into the succeeding module.

As indicated above, one embodiment comprises washing silver halides which have been precipitated in the presence of a peptizer, surfactants or other precipitation aids. The peptizers are added generally to prevent undesirable physical or chemical effects on the grain such as clumping, etc. The precipitation aids or peptizers can be introduced with the respective soluble silver salt and halide salt, or they can be present in the precipitation vessel before precipitation is initiated. It is especially desirable to wash silver halides which have been precipitated in the presence of synthetic peptizers which cannot be washed by procedures described heretofore, such as noodle washing or gelatin coagulation washing.

Any solvent in which the peptizer, silver halide and membrane are compatible can be employed. Aqueous solvents are most preferable, however, solvents comprising most organic acids, ethanol/water mixtures, chloroform, carbon tetrachloride acetone, toluene, dioxane and ethylene oxide can be usefully employed. Should a cellulose acetate membrane be employed, only an aqueous medium can be used.

In another embodiment, an improved process for concentrating photographic melts or emulsions in order to remove excess liquid phase prior to coating is provided. Normally, silver halide emulsion melts are quite dilute due to the addition of various solutions of addenda such as, for example, coating addenda. With the improvements in casting technology, it is now feasible and economically advantageous to remove as much of the liquid phase prior to coating rather than by the slow diffusion-limited machine drying processes which are generally employed. Concentration by ultrafiltration provides a physical separation of the liquid phase from the silver halide emulsion which requires no phase change.

The silver halide emulsions and other photosensitive emulsions can be concentrated to a variety of viscosities; the selection of viscosities being a function of the coating conditions, the material to be coated, the properties of the final photographic product to be produced and the like. Typically, the photographic melts fed into the module have viscosities in the range of from about 1 to about 20 centipoise and the retentates have viscosities in the range of from about 1 to about 200 centipoise, preferably about 1 to 10 centipoise.

The photographic melts and emulsions may be unwashed or washed to remove soluble salts. It is generally preferable to wash the precipitated silver halides, particularly should the silver halides be precipitated in the presence of a synthetic peptizer such as, for example, copoly (3-thiapentylacrylate-3-acryloxpropane-1-sulfonic acid sodium salt) and the like.

EXAMPLE 1 - Washing

A 0.2 micron silver iodobromide (2.5 mole % iodide) emulsion is prepared by simultaneously adding equal molar solutions of potassium halide and silver nitrate solutions to a rapidly agitated aqueous solution containing 11.5 g/silver mole of the copolymer 3-thiapentylacrylate-3-acryloyloxpropane-1-sulfonic acid sodium salt.

A 6 liter sample (1.43 kg/silver mole) is washed three times by concentrating to 1.5 liters and rediluting to 6 liters. The washing is performed at the overall average rate of 0.5 silver mole/hour. The ultrafiltration unit employed is the commercially available modular thin-channel TC-1 manufactured by Amicon Corporation. The unit is typical of that module illustrated in Figure 1. A pressurized aqueous solution of silver halide, peptizer and extraneous salts, (A), (B), is passed through the inlet of the module of Figure 1, the extraneous salts (B) and solvent pass through the membrane while the concentrated solution of peptizer and silver halide (A) is passed out of the outlet. The unit is a single membrane cell containing 1/8 ft^2 of active membrane surface area. The membrane employed is the Amicon PM-30 which has a published "molecular weight cut off" at 30,000 and is commercially available from Amicon Corporation. The initial pAg reads 9.3, the washed emulsion has a pAg of 8.12. The washed emulsion is dispersed in 187 gms. gelatin/silver mole coated at 162 mgs. silver/sq.ft., exposed and processed in the conventional manner. The fog obtained is 0.01 units above the film base density.

EXAMPLE II - Washing

A 0.2 micron silver iodobromide emulsion (1.3 kg/silver mole) is prepared as in Example 1. The peptizer concentration is 11.5 g/silver mole. The emulsion (15 liters) is washed in three cycles, at an overall average rate of 7.7 silver moles/hour by concentrating to 3.75 liters and rediluting to 15 liters. The ultrafiltration unit employed is the American Standard TM5-14 module with cellulose acetate membranes. The initial pAg reads 9.29; the washed emulsion has a pAg of 8.20. The emulsion is dispersed in 187 g gelatin/silver mole and coated at 180 mg. silver/sq. ft. After processing, a gross fog of 0.02 is obtained. Gross fog, as employed herein, is the optical density of an unexposed and processed photographic element and includes the film base density.

EXAMPLE III - Concentrating

A silver iodobromide (6 mole % solid) emulsion is prepared by slowly adding an aqueous solution of silver nitrate to an agitated aqueous solution containing the alkali metal halides and copolymer 3-thiapentyl-acrylate-3-acryloyloxy-propane-1- sulfonic acid, sodium salt. The peptizer concentration is 24 g/silver mole. After precipitation, the emulsion is washed by adding to the emulsion beads of an ion change resin comprising a cation resin and an anion resin. The emulsion is stirred for 5 minutes (pAg = 5.8) and filtered to remove the beads. The washed emulsion is sulfur and gold sensitized in a conventional manner and concentrated from 3.45 kg/silver mole to 1.15 kg/silver mole by employing the Amicon TC-1 module containing the PM-30 membrane. The concentrated emulsion is dispersed in 55 g gelatin/silver mole and coated on a film support at 516 mg silver/ft^2, exposed and developed in a conventional metol-hydroquinone developer, fixed and washed. An excellent photographic image is obtained.

Although the processes of the examples are carried out in discrete concentration/redilution cycles in which the sample is rediluted in the recycle reservoir, the method in which a liquid level controller in the recycle reservoir used to replace filtrate with distilled water continuously can also be used.

Patent applications embodying subject matter disclosed in this report may be pending in one or more countries.

Disclosed anonymously (R1291)
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