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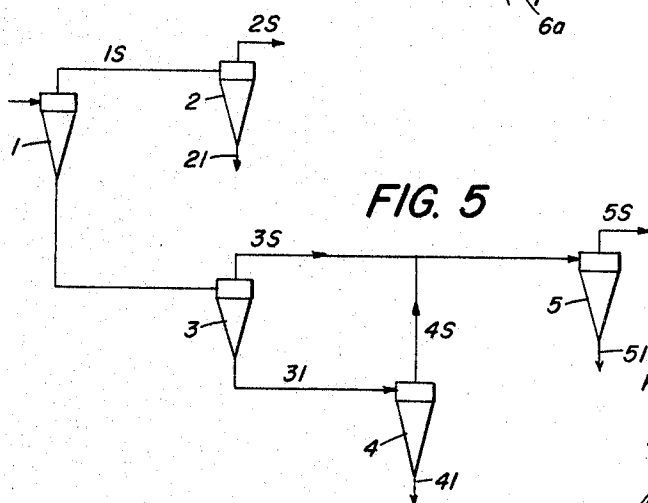
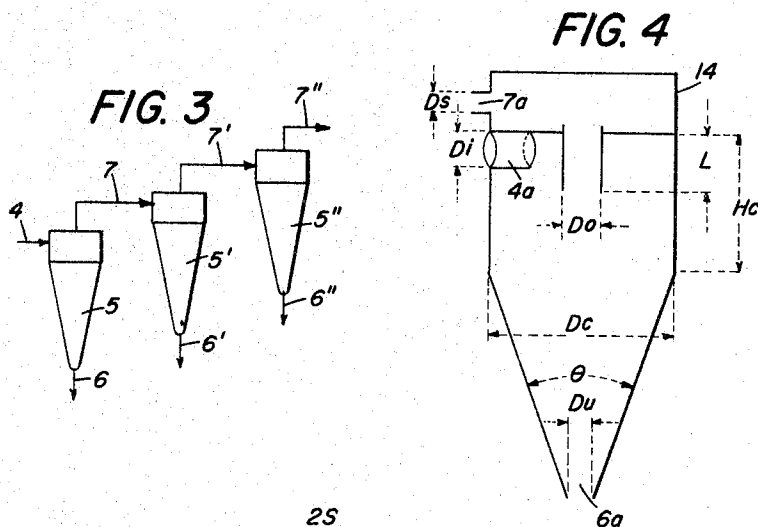
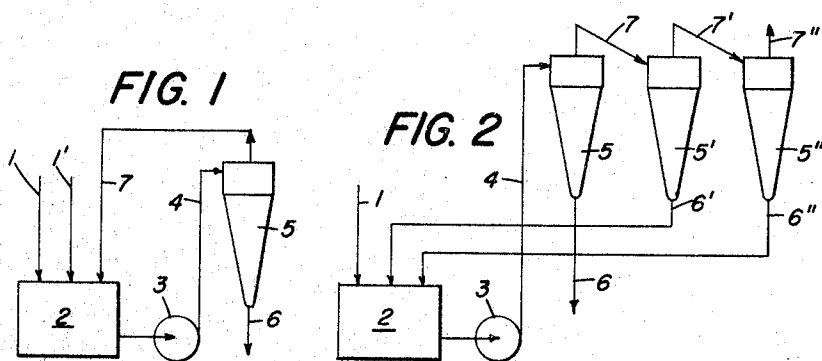
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FRACTIONAL SEPARATION OF SILVER HALIDE GRAINS

Filed Feb. 12, 1964

2 Sheets-Sheet 1



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FIG. 6

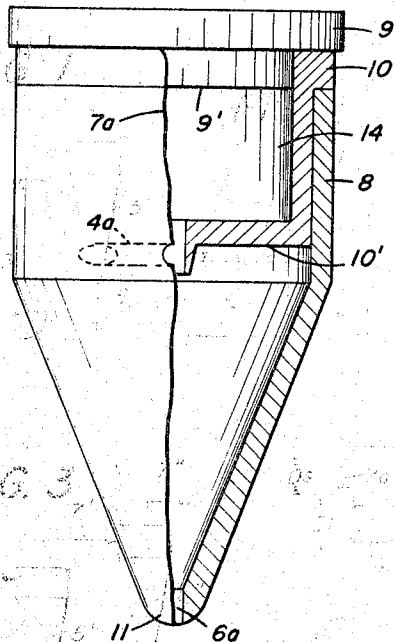
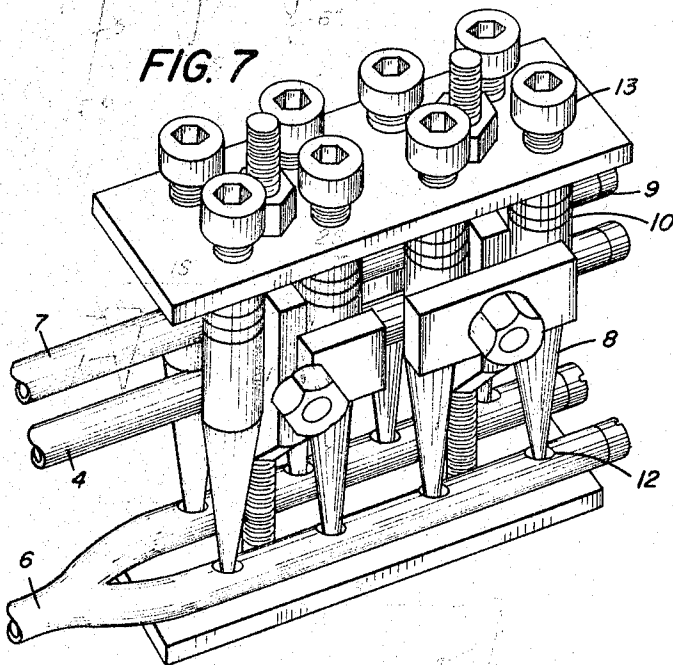


FIG. 7



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FRACTIONAL SEPARATION OF SILVER HALIDE GRAINS

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3 Claims. (Cl. 23-305)

This invention relates to the manufacture of silver halide photographic emulsions which involves classification of the grain size by means of hydrocyclones.

In the course of the conventional preparation of light-sensitive emulsions, it may be desirable to sort-out, according to size, the ripened silver halide crystals in suspension in a colloidal medium, in order, for instance, to separate the large highly sensitive grains and/or the fine insensitive grains.

More generally, it is desirable to be able to prepare, as wanted, homogeneous categories of physically ripened grains whose subsequent application would be more flexible and efficient, irrespective whether the sensitization or coating is contemplated in the form of a mixture or as superposed layers.

The conventional separation processes (sedimentation or mechanical centrifuging) hitherto used for the sorting out of silver halide crystals in the process of formation result in a more or less broad statistical distribution pattern of sizes, narrowing down of which is in most cases indicated; sedimentation requires keeping the dispersion in the liquid phase for long periods of time, thereby increasing fogging propensity, whereas mechanical centrifuging of the colloidal suspension of silver halide crystals whose calibration is not very precise causes grain clumping and deposits, as well as the crushing of grains against the walls of the device, factors that are all prejudicial to the quality of the light-sensitive emulsion, especially in view of the fact that all of these methods tend to fog the silver halide grains. Furthermore, in a continuous manufacturing process, the slow rate of growth of the crystals and the durations of ripening necessitate very long circuits.

The process according to the invention consists in inserting in the manufacturing circuit of the light-sensitive emulsion a ripening zone of suitable volume in which, by application of a field of centrifugal force, the silver halide crystals are maintained in continuous circulation, and from which they are continuously extracted and evacuated as they grow to a set size, the crystals having achieved the said size being immediately removed from the centrifugal force field.

For the purpose of production by the continuous process, those of said crystals that have not achieved the desired size are, if necessary, reintroduced into the circuit comprising the said ripening zone or a plurality of series-connected ripening zones, in order there to continue their growth.

The zones of application of the field of centrifugal force may, according to one embodiment, be linked by means of a cascade-connection for the purpose of separating and classifying crystals of various sizes, with the number of categories depending on the number of zones.

For the application of the process according to the invention, the field of centrifugal force to which the silver halide crystals in suspension are subjected for the purpose

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of separating them into granulometrically different categories without combining the crystals in the form of clumpings or deposits, and without subjecting them to friction and crushing, is created by a hydrocyclone or a set of hydrocyclones mounted on a closed circuit in which a suitable device provides for continuous circulation of the suspension.

In the annexed drawing, given merely by way of example;

FIG. 1 is a partial schematic representation of a device according to the invention for the preparation of light-sensitive emulsions, showing the ripening zone and the generator of the field of centrifugal force.

FIG. 2 is a schematic representation of the same part of another device, according to another application of the process of the invention, wherein the hydrocyclones are shown in cascading-connection, for the separation of grains of one and the same size.

FIG. 3 is a schematic representation of a cascading-connection of three hydrocyclones for the separation of grains of three different categories.

FIG. 4 is a schematic representation of a hydrocyclone on which are indicated the symbols of the various geometric parameters particularly suitable for the treatment of light-sensitive emulsions.

FIG. 5 is a diagram of the treatment equipment according to the invention.

One-half of FIG. 6 is a side-view and one-half is a cross-sectional view of a hydrocyclone according to the invention.

FIG. 7 represents a battery of eight hydrocyclones.

According to one embodiment shown in FIG. 1, the colloidal dispersion of silver halide crystals, whose viscosity is adjusted to a suitable level, is formed in a tank 2 whose volume varies with the equipment discharge and the dispersion characteristics and into which the customary reagents are introduced via the pipes 1, 1'. The colloidal dispersion is discharged under pressure by means of a pump 3 into a pipe 4 extending into the generator of the field of centrifugal force 5, of the type described below, which separates the silver halide crystals into two distinct groups. The crystals having undergone a sufficient ripening and whose size corresponds to that selected for the emulsion to be manufactured are continuously evacuated via a pipe 6, whereas the others, of smaller size, are by means of a pipe 7 reintroduced into the tank 2 and continue growing by mingling with the fresh amount of dispersion formed by the introduction of reagents via the pipes 1, 1'. It can thus be seen that this arrangement of the equipment according to one embodiment of the invention makes it possible, in particular, to produce continuously a light-sensitive emulsion by means of a very short treatment circuit that nevertheless permits the ripening of the silver halide crystals.

According to the embodiment of FIG. 2 the pipe 7 for the removal of the crystals of a size below that desired to be achieved feeds a second generator 5' which, in turn, feeds another generator 5''. The equipment set up according to this arrangement works like a radioelectric band-pass filter: the finest silver halide crystals unsuited for the manufacture of a light-sensitive emulsion are evacuated from the generator 5'' via the pipe 7'', whereas all crystals of a size greater than that of the grains removed via the pipe 7', and smaller than that of the grains evacuated via the pipe 6 (which grains evacuated via pipe 6 constitute the grains having the

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wanted size) are reintroduced via the pipes 6' and 6'' into the tank 2 where they continue their growth mingled with the fresh dispersion initially introduced via the pipe 1. It is quite obvious that one may arrange in groups any number of generators according to this type of connection.

FIG. 3 represents a cascading connection of three generators 5, 5' and 5'' of different characteristics making it possible, respectively, to select grains of decreasing sizes. The discharge pipes 6' and 6'' of the last two generators do not reintroduce the selected grains into the tank 2, not shown. These silver halide crystals of determined and different sizes that are thus separated and retained are used for the manufacture, either by themselves or in mixtures according to well-defined ratios of light-sensitive emulsions having different characteristics. Any number of generators may be arranged in groups in that manner.

FIG. 4 which represents in a schematic cross-section a generator of a centrifugal force field, used according to the process that is the object of the invention, indicates the various geometric parameters determining the proper operation of the generator for the sorting out of the silver halide crystals. The generator utilized according to the invention is a hydrocyclone, a known device, used for the separation of a mixture of two phases at least one of which is liquid.

The excellent results achieved in the preparation of light-sensitive emulsions through the use of hydrocyclones are unexpected and novel. Indeed, as was recalled above, the utilization of a field of centrifugal force generated by mechanical centrifugal machines for the sorting out of silver halide crystals causes grain clumping and deposits, as well as possible fogging through the crushing of grains against the walls. One might have expected to find also the same shortcomings by using hydrocyclones, whereas, on the very contrary, the practice showed that the aforementioned shortcomings disappear.

The suitably diluted liquid dispersion is at a given pressure introduced into the hydrocyclone where it is for an extremely short period of time subjected to the centrifugal force providing for the separation of the grains into two granulometric categories lying on either side of a preset size. This shortened treatment period eliminates the alteration likely to result from extended treatments, as occurs in the sorting-out process by sedimentation. On the other hand, no silver halide material is subjected to the centrifugal force after the separation occurred, contrary to the procedure in mechanical centrifugal machines. The centripetal discharge of the dispersion maintains the grains in the dispersed state and does not promote the formation of deposits and grain clumping, usual sources of fogging; furthermore, it eliminates their crushing against the walls, as a result of which fogging may be produced with emulsions that are vulnerable and of high sensitivity.

The following, non-limiting, example illustrates an application of the manufacturing process according to the invention.

Example

A negative, high-speed, silver bromiodide emulsion containing 12 grams gelatin per mole of silver is diluted to about 5 kg. per mole of silver. Under these conditions, 51 moles of emulsion under a pressure of 150 p.s.i. are introduced into a hydrocyclone whose cylindrical chamber has a diameter of 5 mm. This hydrocyclone is a part of the installation schematically shown in FIG. 5, in which each cyclone works independently.

Following separation within the installation, the emulsion is concentrated by coagulation, then the gelatin is added to produce about 80 grams per mole of silver and the overall weight is adjusted to 1.5 kg. per mole of silver.

The emulsions prepared in this manner from the various fractional amounts discharged by the different hydrocyclones are coated on a support to allow determining of

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the sensitometric characteristics in the customary manner.

These results are recorded in the table below where the different emulsions refer to the number of the hydrocyclone from which they originated followed by the letter S (supérieur=upper) or I (inférieur=lower) depending whether they originate from the material fraction discharged by the upper or lower aperture, respectively.

Emulsion	Total percent-age of emulsion collected	Percent mole Ag I	Radius of largest grain (in μ)	Average area of grains (in μ^2)	γ	Fog
Control	-----	5.2	1.15	0.54	1.20	0.08
2S	30.5	3.5	0.85	0.36	1.80	0.11
2I	15.2	5.0	1.20	0.62	1.51	0.09
4I	41.5	6.2	1.35	2.08	1.65	0.09
5S	4.0	4.2	1.05	0.50	1.75	0.08
5I	8.9	6.1	1.45	1.25	1.45	0.08

An emulsion prepared from grains sorted out according to conventional processes, e.g., by sedimentation, which, as indicated by F. F. Renwick in the British Photographic Journal of Aug. 1924 (p. 362) "creates great problems, for the emulsion has to be kept liquid for long periods of time while making it preserve its photographic qualities during the sedimentation," produces, after treatment, fogs of 0.10 in the case of the emulsion prepared with grains of the upper layer and of 0.22 in the case of the emulsion prepared with grains of the lower layer, fog values considerably greater than those achieved by the process according to the invention. Indeed, the above table indicates that the fog density is, with emulsions treated according to the invention, practically identical to that produced by the identical emulsion that has not been treated.

The use of hydrocyclones offers, besides, great advantages with regard to plant maintenance, for one uses static devices that do not comprise any moving part, whose wear and clogging up are practically zero provided the dispersion has been properly filtered.

Practice proved that all the geometrical parameters determining the properties of the hydrocyclone used for the preparation of photosensitive emulsions can be brought in relationship with the internal diameter D_c of the cylindrical chamber of elevation H_c . D_o and L designate the diameter and the length of the central pipe for separation of the ascending and descending, eddying liquid fluxes, herebelow referred to merely as pipe; and, respectively, D_i the diameter of the input tube 4a, D_s that of the lateral aperture 7a of the evacuation chamber 14, D_u the diameter of the discharge aperture 6a, and θ the angle of the cone of the lower section.

In practice, these parameters must suitably satisfy the following relationships:

$$H_c = \frac{D_c}{2}$$

$$D_i = \frac{D_c}{5}$$

$$D_o = \frac{D_c}{5}$$

$$L = \frac{D_c}{3}$$

$$D_u = \frac{D_c}{15}$$

$$D_s > D_o$$

$$D_o < 10 \text{ mm.}$$

$$\theta \approx 0.157 \text{ rd.}$$

The hydrocyclone designed according to one embodiment of the invention (FIG. 6) comprises a housing 8, plug 9, and a liner 10. The housing 8 and the plug 9 are

made of stainless steel whose grade is suitable for the emulsions treated; the pipe bearing liner 10 is made of plastic capable of precision machining and providing tightness of the assembled unit. The input tube 4a and the lateral aperture 7a of the evacuation chamber 14 are situated on the same outer generatrix of the cylinder; the input tube 4a extends tangentially into the interior of the cylindrical section of the body 8 whereas the lateral aperture 7a is pierced radially. The lower planes 9' and 10' of the plug 9 and the liner 10 are tangential to the pipes 7a and 4a, respectively. The practice proved that the use of small angles of θ , below 0.157 rd., transforms the hydrocyclone into a separator, the hydrocyclone will then separate the liquid phase from the particles in suspension, instead of sorting them out.

In the case of industrial applications it is often necessary to use equipment having a large output. To this end, one may at each separation stage use batteries of hydrocyclones parallel-supplied as shown in FIG. 7. Each one of the hydrocyclones, a total of eight in the example shown, presses firmly against the feeder pipes 4 and the upper discharge pipe 7 by means of an inserted seal, not shown, between each aperture of the hydrocyclone housings and a corresponding aperture of said pipes. The cone of the body 8 of each hydrocyclone ends in a spherical calotte 11 (FIG. 5) to be fitted into a tapered hole 12 of the discharge pipe 6, thus giving the housing 8 a certain degree of angular play indispensable for the flattening of the seals of the pipes 4 and 7. An adjustable pressure screw 13 makes it possible to provide for tight sealing among the hydrocyclone components 8, 9 and 10 and between the housing 8 and the discharge pipe 6.

Assembled in this manner, this hydrocyclone battery supplied under a pressure of 686 k. Pa is capable of processing 120 cubic decimeter/hr. of colloidal silver halide dispersion.

It is well understood that the invention is not limited to the various embodiments described and illustrated which were selected as examples only.

We claim:

1. A method of treating an aqueous dispersion of silver halide grains in the process of ripening which comprises, introducing reagents into a first vessel to form an aqueous dispersion of silver halide grains, running the dispersion under pressure into a hydrocyclone separator whereby the dispersion is subjected to centrifugal force in a zone of the separator, wherein silver halide crystals are further ripened to a selected large size withdrawing the larger silver halide grains from the separator as they are formed, withdrawing and returning the small undeveloped grains to said reagent vessel for mingling with the fresh amount of dispersion formed by the introduction of reagents therein.

2. The method of claim 1 in which the said dispersion is introduced under pressure through a series of hydrocyclone separators in cascading connection whereby the dispersion is subjected to centrifugal force in a zone of each separator, withdrawing the large grains from the system only from the bottom of the first separator as they are formed, returning small grains from the separator to said first reagent vessel.

3. The method of claim 1 in which the said dispersion is introduced into a series of hydrocyclone separators in cascading connection withdrawing from the system grains from the bottom of each of said hydrocyclone separators whereby the silver halide grains are separated into different categories of grains of a given size.

References Cited

UNITED STATES PATENTS

2,620,264	12/1952	Watson	23—305
2,707,669	5/1955	Houston	23—273
2,819,154	1/1958	Frejaques	23—273
3,202,487	8/1965	Domning	23—295

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