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3,672,900
FOGGED, DIRECT-POSITIVE EMULSION PRODUCTION BY INCREASED FLOW OF SILVER HALIDE-FORMING PRECIPITANTS IN GRAIN-RIPENER-FREE ACIDIC MEDIUM

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ABSTRACT OF THE DISCLOSURE

A process is disclosed for making improved, fogged, direct-positive, silver halide emulsions. The silver halide grains of said emulsions are made by forming grains of at least 0.4 micron in size in a precipitation medium which is substantially free of ripening agents and wherein the flow rates of the respective reactants to form said silver halide grains are gradually increased during the growth of said grains. Preferably, the pH is maintained at less than 4 and an oxidizing agent is present during the formation of the grains.

This invention relates to new processes of making fogged, direct-positive silver halide emulsions and to the products produced thereby. In one aspect, this invention relates to a process of making high-speed, high contrast, direct-positive emulsions which have an average grain size of above .4 micron and preferably above .7 micron. In another aspect, this invention relates to a rapid process of making a large-grain, direct-positive emulsion wherein the grains are substantially free of reduction sensitization.

It is known in the prior art to make fogged, direct-positive emulsions such as systems disclosed in Illingsworth, U.S. Pats. 3,501,305, 3,501,306 and 3,501,307 and systems wherein the fogged grains contain internal sites for the deposition of photolytic silver such as disclosed in Berriman, U.S. Pat. 3,367,778, issued Feb. 6, 1968. It is also known in the art that when larger grains are desired for direct-positive emulsions they can be made in the presence of thioether ripening agents to obtain a monodispersed large-grain emulsion such as disclosed in Jones, U.S. application Ser. No. 701,092, filed Jan. 29, 1968 corresponding to U.S. Pat. 3,574,628, issued Apr. 13, 1971. However, many of the methods for making large-grain, direct-positive emulsions introduce limitations in the photographic response characteristics of the emulsions which are detrimental in certain uses of the photographic elements made with these emulsions, especially when the processes are scaled up to produce commercial quantities of the direct-positive emulsions. Therefore, it would be desirable to develop improved processes which would produce high-speed, high-contrast, fogged, direct-positive silver halide emulsions.

I have now found that improved large-grain, fogged, direct-positive emulsions can be made by forming the silver halide grains in the absence of a ripening agent at a low pH in the presence of an oxidizing agent wherein the flow rates of the liquid reactants to the precipitation are increased over the duration of growth of the silver halide grains. The direct-positive emulsions containing fogged grains made by this process are generally high-speed, high-contrast emulsions compared to the direct-positive emulsions containing grains of 0.2 to 0.3 micron in size. The ability to make large grains in the order of about 1/2 micron in size and preferably at least 0.7 micron in size in the absence of ripening agents, but in short precipitation times of precipitation in the absence of ripening agents of responds more efficiently when fogged and used in a di-

rect-positive system. Moreover, the low pH and the use of an oxidizing agent apparently reduce the level of reduction sensitization which may be partially responsible for the relative lower speed and lower contrast obtained with many of the prior direct-positive systems. The short times of precipitation in the absence of ripening agents of a large-grain emulsion which is quite monodispersed is, of course, believed to be a contributing factor to the improved properties, as there is less time for random sites to form in some of the grains which could change the photographic characteristics of the respective grains.

In one embodiment of this invention, the silver halide grains are formed by a process wherein the flow rates of the liquid containing the silver ions and the liquid containing the halide ions are increased during the growth of the grains after nucleation and the precipitation vessel is preferably substantially free of silver halide ripening agents. The precipitation can, of course, be stopped at any stage and continued with only a portion of the crystals formed if the size of vessel utilized is restricted to one which will not hold the total liquid addition necessary to form a large-grain emulsion.

In another embodiment, the silver halide grains are formed by either stepwise increasing or gradually increasing the flow rates of the liquid containing the silver ions and the halide ions according to the formula:

$$at^2 + bt + c$$

wherein t equals time of precipitation and a , b and c are constants dependent on factors such as, for example, temperature, concentration, metal ion concentration and the like, and wherein said constants can be derived theoretically or preferably are derived empirically for the particular conditions of operation. The constants are preferably determined for a value wherein new nuclei will not form after initial precipitation whereby all grains will generally grow at the same rate to produce a mono-dispersed emulsion.

In another preferred embodiment, the liquid flow rates of the respective silver halide reactants are gradually increased to the precipitation vessel and the pH in said vessel is controlled at a pH of less than 4 and preferably less than about 2 and an oxidizing agent is present in the precipitation vessel during the formation of the silver halide grains.

In still another preferred embodiment, metal ion dopants are occluded inside the grain during the formation of the grain and preferably iridium ions, bismuth ions and/or lead ions are incorporated in the grains.

In still another embodiment, the grains made by the above processes are reduction and gold fogged to make a direct-positive silver halide emulsion.

In still another preferred embodiment, the flow rates of the reactant salts are increased during the precipitation at a rate not to exceed the maximum flow rate at any respective grain size wherein a substantial amount of new nuclei will form after initial precipitation has commenced and wherein the flow rate is increased by a factor wherein the precipitation time to produce a given grain size is reduced by at least 50% over similar precipitations wherein the flow rates are constant throughout precipitation.

Typical useful direct-positive systems which can be made using the improvements of this invention include:

(1) Emulsions containing fogged silver halide grains which have internal centers for the deposition of photolytic silver such as those generally disclosed in Berriman, U.S. Pat. 3,367,778, issued Feb. 6, 1968, including emulsions comprising grains which have centers which promote the deposition of silver which are either sufficiently small or sufficiently buried within the crystal as to be

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not accessible to initiate surface development to a visible image. Silver halide grains of this latter type can be provided by using very low concentrations of metal dopants or sensitizing agents throughout the precipitation, or adding the metal dopant to the precipitation medium during the initial part of the precipitation.

(2) Emulsions which contain silver halide grains which are uniformly fogged to specific levels and contain electron-accepting compounds adjacent the grains, as described in Illingsworth, U.S. Pat. 3,501,305, issued Mar. 17, 1970.

(3) Emulsions comprising fogged regular grains which contain an electron-accepting compound or desensitizer adjacent the grains, as described in Illingsworth, U.S. Pat. 3,501,306, issued Mar. 17, 1970.

(4) Emulsions comprising monodispersed grains which have been reduction and gold fogged, as described in Illingsworth, U.S. Pat. 3,501,307, issued Mar. 17, 1970.

The silver halides employed in the preparation of the photographic compositions described herein include any of the photographic silver halides as exemplified by silver bromide, silver chloride, silver chlorobromide, silver bromiodide, silver chlorobromide, and the like. Silver halide grains having a mean grain diameter, i.e., an average grain size in the range of about .01 to about 2 microns, preferably about .02 to about 1 micron, give particularly good results in reversal systems. The silver halide grains can be any suitable shape such as cubic or octahedral, but they are preferably cubic, and more preferably cubic-regular. The preferred photographic silver halide emulsions comprise at least 50 mole percent bromide, the most preferred emulsions being silver bromiodide emulsions, particularly those containing less than about 10 mole percent iodide. The photographic silver halides are generally coated at silver coverages in the range of about 50 to about 500 milligrams of silver per square foot of support.

The direct-positive photographic silver halide emulsions made in accordance with this invention contain silver halide grains which are fogged. Fogging can be effected by chemically or physically treating the photographic silver halides by methods previously described in the prior art. Such fogging can be accomplished by various techniques such as chemical sensitization to fog, particularly good results being obtained with techniques of the type described by Antoine Hautot and Henri Saubenier in *Science et Industries Photographiques*, vol. XXVIII, January 1957, pages 57-65. The silver halide grains can be fogged with the high-intensity light, reduction fogged with a reducing agent such as thiourea dioxide or stannous chloride or fogged with gold or noble metal compounds. Combinations of reduction fogging agents with gold compounds or compounds of another metal more electro-positive than silver, e.g., rhodium, platinum or iridium, can be used in fogging the silver halide grains. The fogged silver halide grains in the direct-positive photographic emulsions of this invention give a density of at least 0.5 when developed without exposure for 5 minutes at 68° F. in Kodak DK-50 developer when a direct-positive emulsion containing such grains is coated at a coverage of 75 to about 500 mg. of silver per square foot of support.

The direct-positive photographic emulsions of this invention can comprise reduction and gold fogged silver halide grains, i.e., silver halide grains which are fogged with a combination of a reduction fogging agent and a gold fogging agent. The use of low concentrations of reduction and gold fogging agents in such a combination give unique fogged silver halide grains which are characterized by a rapid loss of fog upon chemical bleaching. It is known that 1 equivalent weight of a reducing agent will reduce 1 equivalent weight of silver halide to silver. To obtain the fogged silver halide grains which are characterized by a rapid loss of fog upon bleaching, much less than 1 equivalent weight of reduction fogging

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agent is employed. Thus, less than about 0.06 milliequivalent of reduction fogging agent per mole of silver halide is employed in fogging the silver halide grains. Generally, about 0.00025 to about 0.06, preferably about 0.0005 to about 0.03 milliequivalent of reduction fogging agent per mole of silver halide is employed in fogging the silver halide grains in the practice of this invention. Higher concentrations of reduction fogging agent can result in a substantial loss in photographic speed. A preferred reduction fogging agent employed in combination with the gold fogging agent, or a compound of another metal more electropositive than silver, is thiourea dioxide which is preferably employed in a concentration in the range of about 0.01 to about 3, most preferably about 0.05 to about 2, mg. per mole of silver halide or about 0.0001 to about 0.03 millimole per mole of silver halide. Stannous chloride is another suitable reduction fogging agent which is used in practicing this invention and is preferably used in concentrations in the range of about 0.05 to about 3 mg. of stannous chloride per mole of silver halide. The use of the reduction and gold fogging agents in low concentration gives direct-positive photographic silver halide emulsions exhibiting outstanding photographic speed. Examples of suitable reduction fogging agents which can be employed in the practice of this invention include hydrazine, phosphonium salts such as tetra(hydroxy methyl)phosphonium chloride, thiourea dioxide as disclosed in U.S. Pats. 3,062,651 by Hillson, issued Nov. 6, 1962, and 2,983,609 by Allen et al. issued May 9, 1961, reducing agents such as the stannous salts, e.g., stannous chloride, as disclosed in U.S. Pat. 2,487,850 by Carroll, issued Nov. 15, 1939, polyamines such as diethylene triamine as disclosed in U.S. Pat. 2,519,698 by Lowe et al. issued Aug. 15, 1950, polyamines such as spermine as disclosed in U.S. Pat. 2,521,925 by Lowe et al. issued Sept. 12, 1950 bis(β -aminoethyl) sulfide and its water-soluble salts as disclosed in U.S. Pat. 2,521,926 by Lowe et al. issued Sept. 12, 1950, and the like.

The gold fogging agents employed in practicing this invention can be any gold salt suitable for use in fogging photographic silver halide grains and includes the gold salts disclosed in U.S. Pats. 2,399,083 by Waller et al. issued Apr. 23, 1946, and 2,642,361 by Damschroder et al. issued June 16, 1953. Specific examples of gold fogging agents are potassium chloroaurate, alkali metal aurous thiosulfates, aurous sulfide, potassium aurithiocyanate, potassium chloroaurate, auric trichloride, 2-aurousulfobenzothiazole metho chloride, and the like. The concentration of gold fogging agent employed in the practice of this invention is subject to variation, but is generally in the range of about 0.001 to about 0.01 millimole per mole of silver halide. Potassium chloroaurate is a preferred gold fogging agent and is often used at concentrations of less than about 5 mg. per mole of silver halide and preferably at concentrations in the range of about 0.5 to about 4 mg. per mole of silver halide.

Preferably, the direct-positive emulsions used in this invention contain electron-accepting compounds, often referred to as desensitizers or electron traps, which are generally compounds having an anodic polarographic half-wave potential and a cathodic polarographic potential which, when added together, give a positive sum. Typical useful electron-accepting compounds, along with methods of determining the polarographic potentials, are disclosed in the above-mentioned applications on direct-positive emulsions, as well as in Illingsworth et al., U.S. Pat. 3,501,310, issued Mar. 17, 1970. An especially useful class of electron acceptors which can be used in the direct-positive photographic silver halide emulsions and processes of this invention are cyanine dyes such as the imidazo[4,5-b]quinoxaline dyes. Dyes of this class are described in Brooker and Van Lare, U.S. Pat. 3,431,111, issued Mar. 4, 1969. In these dyes, the imidazo[4,5-b]-

quinoxaline nucleus is attached, through the 1-carbon atom thereof, to the methine chain.

The direct-positive emulsions of this invention also can contain compounds referred to as halogen-accepting or halogen-conducting compounds, especially if the halide of the emulsion is a high chloride emulsion. Useful compounds of this type are generally characterized by an anodic polarographic potential less than 0.85 and a cathodic polarographic potential which is more negative than -1.0. Highly preferred species of compounds of this type are merocyanine dyes having the above halfwave potentials. Typical compounds of this type, along with methods of determining the polarographic potential, are disclosed in the above-mentioned applications on direct-positive emulsions as well as in Wise, U.S. Ser. No. 615,360, filed Feb. 13, 1967 corresponding to U.S. Pat. 3,537,858, issued Nov. 3, 1970.

In the process of precipitation of the silver halide according to the invention, the pH and/or pAg (silver-ion concentration) are generally monitored and controlled by apparatus known in the art. Typical useful control apparatus are disclosed in U.S. Pat. 3,031,304 and in F. H. Claes and W. Peelaers, "Crystal Habit Modification of AgBr by Incorporation of I-Ions," Photographische Korrespondenz, 103-161, 1967. Automatic control apparatus of this type can be used to control the pH and/or pAg of the emulsion within a range of ± 0.02 unit after the first few seconds of the precipitation start-up procedure. In accordance with the invention, the total precipitation procedure can be carried out in an interrupted manner, a continuous manner or a semicontinuous manner.

The pAg of the system is determined by methods commonly used in the trade and is the negative logarithm of the silver ion concentration expressed as moles per liter. The general formula for the determination is as follows:

$$pAg = \log \frac{1}{[Ag^+]}$$

wherein Ag^+ is the silver-ion concentration. In a typical embodiment, the pAg may be measured by conventional techniques such as, for example, by measuring the difference between a reference electrode and the pAg electrode which can be a silver electrode.

In preferred embodiments, this process can be used to make monodispersed crystals. Generally, in such emulsions no more than about 5% by weight or number of the crystals smaller than the mean grain size and/or no more than 5% by weight or number of the crystals larger than the mean grain size vary in diameter from the mean grain size by more than 25% and preferably no more than 10%. The grain size can be determined by means commonly used in the art which include projective area, electron-microscopy and the like. The size distribution can also be readily calculated as the variation coefficient which is equal to the standard deviation times 100 divided by the average grain-edge length. Generally, the process of this invention can be controlled to provide a variation coefficient of less than 20 ± 5 and preferably less than 10 ± 4 .

In one typical batch precipitation procedure, the crystals can be formed by a double-jet apparatus wherein the precipitation vessel is in the shape of a bowl with upwardly extending diverging walls. The diverging-wall container will accommodate small volumes during the initial nuclei formation and will also be adequate to contain the medium under increased flow conditions. A stirrer or agitator can be employed in the vessel and preferably a device such as disclosed in Frame and Johnson, U.S. Pat. 3,415,650, can be used. The flow rates can be controlled by peristaltic-type pumps which are in turn hand-controlled or preferably controlled with a continually monitoring proportional controller. The ion concentration can be measured by methods used in the art.

The flow rate of the various reactants which form the desired metal salt crystals can be increased during the course of the precipitation by any predetermined schedule

depending on the desired result. In accordance with this discovery, it has been found that an increase in the flow rates of the respective reactants will produce large grains in shorter precipitation times than has been possible with prior-art techniques.

In one embodiment, the flow rates of the reactants are controlled according to the formula:

$$at^2 + bt + c$$

wherein t equals time of precipitation and a , b and c are constants dependent on temperature, concentration, metal-ion concentration, vessel size and the like. The constants of this equation can be derived theoretically, but they are preferably derived empirically for the particular apparatus and conditions utilized for precipitation. Generally, the constants can be determined by running a precipitation and by taking periodic samples; one can plot the points for various conditions wherein substantial new nucleation takes place. The equation for the curve can then be calculated for the optimum flow rates at any given time without instituting substantial new nucleation. In one particular preferred procedure for precipitating silver halides, the flow rates are increased by at least about 20% over the duration of a continuous precipitation for an average grain size of above 0.5 micron, at least about 100% for an average grain size of above 1.5 microns, and at least 200% for an average grain size of above 3.0 microns. However, it is understood that improvements in uniform grain growth can be obtained with any increase in flow rates of the respective reactants to the precipitation vessel as long as the rate of increase is not surpassed wherein substantial new nucleation is initiated. Likewise, in one highly preferred embodiment, the respective increase in flow rates is controlled at a rate below that which will initiate substantial new nucleation, but they are at least increased by a factor wherein the time necessary to produce a given grain size is reduced by at least 50% over similar precipitations wherein the flow rates are held constant throughout the duration of the precipitation.

The formation of the silver halide grains is preferably carried out in the presence of an oxidizing agent. Generally, the amount of oxidizing agent incorporated in the precipitation vessel is from about 0.005 to about 0.50 weight percent, based on the total weight of the precipitation medium, and preferably about 0.05 to about 0.10 weight percent. Generally, the amount of oxidizing agent is increased as the volume increases in the precipitation vessel such as by introduction along with one of the reactants or by a separate inlet flow to control the pH. Typical useful oxidizing agents include nitric acid, n-bromosuccinimide, dinitrogen tetroxide, bromine, chlorine and the like.

The precipitation vessel is preferably substantially free of a silver halide ripening agent during the formation of the silver halide grains. Silver halide ripening agents such as ammonia, thiocyanates, thioethers and the like apparently affect the grain structure in such a way as to affect detrimentally some of the photographic properties of direct-positive emulsions.

The actual precipitation can be carried out in the presence of various peptizers, surfactants or precipitation aids to prevent undesirable physical or chemical effects on the grains such as clumping, etc. In certain embodiments, precipitation aids or peptizers can be introduced with the respective injection of the metal cation or the anion of the salt to be precipitated, or they can be present in the vessel before precipitation is initiated. In the instance of silver halide precipitation, it is generally preferred to carry out the precipitation in the presence of a peptizer such as gelatin, synthetic polymeric peptizers such as hydrophilic polymers as disclosed in Perry et al., U.S. Pat. 3,425,836, issued Feb. 4, 1969, acrylyl or methacrylyl histidine polymers such as disclosed in U.S. Pat. 3,419,397, issued Dec. 31, 1968, hydrophilic poly-

mers such as disclosed in Whitely et al., U.S. Pat. 3,392,025, interpolymers containing vinylamine units as disclosed in Smith et al., U.S. Pat. 3,415,653, issued Dec. 10, 1968, interpolymers such as disclosed in Hollister, U.S. Ser. No. 701,114, filed Jan. 29, 1968 corresponding to U.S. Pat. 3,536,677, issued Oct. 27, 1970, interpolymers as disclosed in Smith et al., U.S. Ser. No. 701,084, filed Jan. 29, 1968 corresponding to Belgian Pat. 727,604, issued Mar. 31, 1969, and the like.

The silver halide salts produced in accordance with this invention can be washed, if desired, to remove the soluble salts. Typical useful procedures involve chill-setting and leaching or coagulation-washing, e.g., by the procedures described in U.S. Pats. 2,618,556 by Hewitson et al., 2,614,928 by Yutzy et al., 2,565,418 by Yackel, 3,241,969 by Hart et al. and 2,489,341 by Waller et al.

When silver halides are produced by this method, the normal addenda useful in photographic silver halides can be added to the emulsion after completion of precipitation or during the final stages of precipitation, such as chemical sensitizers, spectral sensitizers, development modifiers, antifoggants, developing agents, hardeners, coating aids and the like.

The invention can be further illustrated by the following examples.

EXAMPLE 1

A double-jet silver bromide precipitation is carried out using an automatic control apparatus wherein the pH is maintained at 2.0 with nitric acid and the pAg is maintained at 8.2 throughout the precipitation. The initial flow rates are 4 ml./minute of a 2.66 molar silver nitrate solution and 4 ml. of a 2.66 molar halide solution, and the flow rates are gradually increased to a flow rate of 120 ml./minute, respectively. The resulting grains have an edge length of 0.472 micron after a run time of 72 minutes.

Of the grains precipitated, 12.5 percent are used as nuclei for a second precipitation with the same apparatus. The respective flow rates are stated at 16.2 ml./minute and increased to 62.8 ml./minute by the end of 95 minutes. The pH is again maintained at 2.0 with nitric acid and the pAg is maintained at 9.8. The resultant grains have an average edge length of 0.975 micron.

A run of about 133 hours would be necessary to build up grains of similar size in similar environmental conditions if the flow rates were not increased.

EXAMPLE 2 (CONTROL)

A silver bromoiodide emulsion is prepared similar to that described in Musliner, U.S. application Ser. No. 31,351, filed Apr. 23, 1970 corresponding to Belgian Pat. 766,236, issued Oct. 25, 1971, at a pH of 5.6 and a pAg of 8.7. The precipitation medium contains 100 mg./silver mole of the ripening agent 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane as described in U.S. Pat. 3,062,646. The cubic silver halide grains have an edge length of 0.93 micron.

EXAMPLE 3

The emulsions of Examples 1 and 2 are tested for internal sensitivity to show the difference in grain formation. The respective unsensitized emulsions are coated on a film support, exposed for $\frac{1}{60}$ second using a 500-watt tungsten source on a Bausch and Lomb sensitometer and developed for 6 minutes in an Elon-hydroquinone developer containing 0.5 g./liter of potassium iodide.

TABLE 1

Example number	pH during precipitation	Internal development D_{min}
1-----	2.0	.05
2-----	5.6	.84

The above table shows that the emulsion precipitated at a high pH results in a high level of internal fog while

the emulsion precipitated at a low pH has essentially no internal fog.

EXAMPLE 4

The emulsions as described in Examples 1 and 2 are then chemically fogged at the surface of the grains by adding 0.1 mg. of thiourea dioxide per silver mole and 0.5 mg. of potassium chloroaurate per silver mole and heated to 60° C. and held for an appropriate length of time to obtain approximately 95 percent fog. The electron-accepting dye described in Belgian Pat. 695,356 as 1,3 - diallyl - 2 - [2 - (3,5-dimethyl-1-phenyl-4-pyrazolyl) vinyl]-imidazo[4,5-b]quinoxalinium iodide is added to each emulsion at 100 mg./silver mole. The emulsions are then coated on a film support at 400 mg. of silver/ft.². After exposing for 1 second with a 500-watt tungsten lamp in a Bausch and Lomb spectrograph, development for 6 minutes in an Elon-hydroquinone developer, fixing and washing, the following results are obtained.

TABLE 2

Example number:	Relative speed
1 -----	174
2 -----	100

It can be seen that the emulsion of Example 1, prepared free of internal fog, has substantially higher speed than the emulsion of Example 2 which has internal fog.

Similar improvements are obtained when metal dopants such as trivalent or tetravalent metal ions are present during the precipitation of the silver halide grain, especially when iridium ions, osmium ions and bismuth ions are present during the silver halide precipitation.

EXAMPLE 5

This example shows that the emulsions prepared by the present process have much higher speed and contrast than a similar emulsion prepared according to Illingsworth, U.S. Pat. 3,501,305.

A 0.2-micron bromoiodide (2.5 mole percent iodide) is prepared and fogged as described in Illingsworth, U.S. Pat. 3,501,305, Example 1, Emulsion A. To the emulsion are added 100 mg. of 1,3-diallyl-2-[2-(3,5-dimethyl-1-phenyl-4-pyrazolyl)vinyl]imidazo[4,5-b]quinoxalinium iodide per silver mole. The emulsion is then coated on a film support to produce equivalent D_{max} of about 2.0, exposed on an Eastman 1B Sensitometer, developed for 6 minutes in an Elon-hydroquinone developer, fixed, washed and dried. The following results are observed when compared to an emulsion of Example 1 processed as described in Example 4.

Emulsion	Precipitation time (minutes)	Grain size (microns)	Relative speed	Contrast
Prior art-----	35	0.2	100	2.02
Examples 1 and 4-----	167	0.975	347	3.00

The 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.

I claim:

1. In a process for making a silver halide, direct-positive emulsion comprising fogged silver halide grains by reacting a water-soluble silver salt with a water-soluble halide in an acidic precipitation medium, and fogging the silver halide grains, the improvement comprising forming silver halide grains of at least 0.4 micron in size in said precipitation medium which is substantially free of a ripening agent and wherein the flow rates of the respective reactants to form said silver halide grains are gradually increased during the growth of said grains wherein the pH is maintained at less than 4.

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2. A process according to claim 1 wherein an oxidizing agent selected from the group consisting of nitric acid, n-bromosuccinimide, dinitrogen tetroxide, bromine and chlorine is present in the precipitation medium.

3. A process according to claim 1 wherein trivalent or tetravalent a metal ion dopant is occluded within said grain during the formation of the silver halide grain.

4. A process according to claim 1 wherein gelatin is present in the precipitation medium.

5. A fogged, direct-positive emulsion produced by the process of claim 1.

6. A process according to claim 2 wherein said oxidizing agent is nitric acid.

7. A process according to claim 1 wherein said increase in flow rates of the respective reactants is controlled at a rate below that which will initiate substantial new nucleation.

8. A process according to claim 1 wherein said fogged silver halide grains are reduction and gold fogged.

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References Cited

UNITED STATES PATENTS

3,501,305 3/1970 Illingsworth 96—108

FOREIGN PATENTS

1,804,289 8/1969 Germany 96—94

OTHER REFERENCES

Hirata and Hohnishi: "Growth Mechanism of Mono-Disperse AgBr Microcrystals in Gelatin Solution," Bulletin of the Society of Scientific Photography of Japan, No. 16, December 1966 (pp. 1-7).

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