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(71) Applicant: **E.I. DU PONT DE NEMOURS AND COMPANY**
1007 Market Street
Wilmington Delaware 19898(US)

(72) Inventor: **Wilhite, Douglas Lee**
1105 Piper Road
Wilmington Delaware 19803(US)

(72) Inventor: **Mickewich, Daniel James**
2005 Millers Road
Wilmington Delaware 19810(US)

(74) Representative: **Werner, Hans-Karsten, Dr. et al,**
Deichmannhaus am Hauptbahnhof
D-5000 Köln 1(DE)

(54) **Splash-prepared silver halide emulsions with a uniform particle size distribution.**

(57) Silver halide emulsions with a narrow and uniform particle size distribution are made by introducing monodisperse seed crystals into a gelatin-salts mixture, followed by normal splash-preparation procedures to make the final emulsion.

Croydon Printing Company Ltd.

TITLE

SPLASH-PREPARED SILVER HALIDE EMULSIONS WITH A UNIFORM PARTICLE SIZE DISTRIBUTION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the field of silver halide emulsion manufacture and particularly to silver halides made by the so-called "splash-precipitation" methods. Still more particularly, this invention relates to a method for making splash-prepared silver halide emulsions with a uniform particle size distribution of the silver halide crystals.

2. State of the Art

Preparation of sensitive silver halides for a photographic emulsion is a complex process. Basically the silver halide crystals or grains can be prepared by two well-known methods: the single jet or "splash" method or the double jet or balanced double jet (BDJ) method. In the splash method, all of the alkali halide solution is placed in the mixing vessel together with the protective colloid (e.g., gelatin) right from the start and the silver nitrate solution is then added to this mixture. The silver nitrate can be added all at once, gradually over a period of time or in several, finite "splashes". In the BDJ method, the halide solution and the silver nitrate solution are added simultaneously to a solution of gelatin in the mixing vessel.

The splash precipitation process usually creates an increased number of so-called "crystal lattice defects" in which a number of ions are not positioned correctly in the silver ion - halide ion network. Emulsions made from these crystals can be used to make films which exhibit improved sensitometry, especially improved speed, as compared with films made from silver halide emulsions with crystals that have few or no lattice defects or disorientation. In spite of this advantage, it is difficult to make splash-prepared emulsions with a uniform distribution of particle sizes. In some areas of photography it is important that emulsions have this uniform distribution in order to control gradient, for example. Thus, in the graphic arts field, a high gradient is necessary and a wide distribution of particle sizes is not tolerable.

On the other hand production of silver halide crystals by the BDJ process will yield grains having good uniformity of particle size but these grains generally lack the disorientation or lattice defects and thus will not be as inherently fast as splash-prepared emulsions.

It is also known to use a seed emulsion with a known particle size, said seed emulsion or crystal being added during the preparation of BDJ emulsions. The silver halide then forms on these seeds and produces a uniform final grain. This process has not been used for the splash preparation of grains since it was thought that uniform grains with high internal defects could not be produced.

SUMMARY OF THE INVENTION

This invention is directed to a process for preparing silver halide emulsions with a narrow grain size distribution, wherein silver nitrate is added by a splash method to an aqueous solution containing (a) one or more alkali halides in a protective colloid, and (b) monodisperse silver halide seed crystals.

The addition of monodisperse seed crystals, themselves made by the BDJ process, to a gelatin-alkali metal halide solution prior to the addition of the silver nitrate by the splash process, achieves the best of both processes. The resulting distribution of crystal sizes is more monodisperse than usually obtained by the splash process, but the crystals are still highly disordered. The grain size and distribution are uniform and predictable, controlled by the size, number, and distribution of the seed crystals in the gel salts, and by the total amount of silver added during the splash process. Thus it is possible to vary the grain size distribution predictably in a splash-prepared emulsion by simply preparing the seed crystals by a BDJ process, which process itself produces a narrow range of particle sizes. A combination of the two precipitation procedures is made possible following the teachings of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The process of this invention is applicable to the manufacture of any of the conventionally prepared silver halides such as silver bromide, chloride, iodide, or mixtures thereof. Any of the conventional colloid binder systems such as gelatin may also be used, as well as water-permeable or water-soluble polyvinyl alcohol and its derivatives, partially hydrolysed polyvinyl acetates, polyvinyl ethers, etc. Other useful colloid binding agents include partially hydrolysed gelatin, poly-N-vinyl lactam, etc. among others. Gelatin is preferred since it is well known that it is the protective colloid of choice during precipitation of the silver halides and the formation of the crystals thereof.

Conventionally, the desired alkali metal halides (salts) are added to an aqueous dispersion of gelatin. One then adds the desired amount of silver halide seed crystals of the desired size already prepared by a BDJ process, and commences stirring. At a desired time and temperature, aqueous silver nitrate is added by the splash method. This may be accomplished with two quick splashes of about 30 seconds each in duration, by one long first splash followed by a quick splash, or by a single long splash. These procedures are well known to those skilled in the art. In yet another embodiment some of the alkali metal halide can be added to the gelatin in the reaction vessel and the remainder added after some of the silver nitrate has been added.

The seed crystals, as previously stated, are made by the BDJ process following those well-known procedures. By varying those procedures it is possible to make grains of any average particle size distribution and select one to be used as desired in the ambit of this invention. The seed crystals can be also made of any of the conventional halides such as silver bromide, silver iodobromide, silver bromo-chloride and silver iodide, for example, Additionally, these seed crystals may be doped with other metals such as rhodium and lead, for example, as is well known.

After the silver halides have been precipitated it is conventional to ripen the emulsion further to achieve the desired crystal sizes. After this point, the emulsion is further "bulked" with colloid binder, and chemical and spectral sensitization can be accomplished as is well known. Following the sensitization step, hardeners, wetting agents, antifoggants, stabilizers, coating aids, etc. may be added. The emulsion can then be coated on any of the well-known photographic substrates such as, for example, polyethylene terephthalate film, suitably subbed (subcoated) to receive the silver halide emulsion coating. The coated emulsion may be overcoated with a protective antiabrasion layer, such as hardened gelatin. These films may be used in any of the conventional ways, for example, as X-ray or graphic arts films or as direct positives. It all depends on the way the product structure is manufactured.

This invention will now be illustrated by the following specific examples of which Example 6 is considered to represent the best mode.

EXAMPLE 1

Four samples of silver halide seed crystals were prepared following standard, BDJ procedures. The halide composition and the average particle size as determined by a Silver Halide Electrolytic Particle Size Analyzer, (Ref. A. B. Holland and J. R. Sawers, Photogr. Sci. Eng. 17, 295 (1973) was as follows:

Sample	Halide	Particle Size (μ^3)
1.	Bromide	0.02
2.	Bromide	0.06
3.	Iodobromide (1% I)	0.03
4.	Iodobromide (1% I)	0.06

These seed crystals of silver bromide and Ag(I)Br, each containing a small amount of bone gelatin from the precipitation process, were redispersed by stirring in gelatin and water for about 3 hours and the pH adjusted to about 6.3-6.7. These seeds were then used at approximately 0.09 moles per 0.51 moles of added silver nitrate (18%) to seed emulsions made by the splash technique using the following solutions and procedure:

A. Solution:	7	g	gelatin
	120	cc	deionized water
	52	g	NH_4Br
	20	cc	0.5 M KI
	0.06	units	Seeds from above
B. Solution:	140	cc	deionized water
	45	cc	3.0 M $AgNO_3$
	30	cc	12.0 M NH_4OH
C. Solution:	70	cc	deionized water
	125	cc	3.0 M $AgNO_3$
D. Solution:	23	cc	glacial acetic acid
E. Solution:	10	cc	coagulant (a poly-anion, see U.S. 2,772,165)
G. Solution:	120	cc	3 M H_2SO_4

Solution A was placed in a mixing vessel and heated to 105°F with stirring. Solution B was then added to A over a 30 second period (first "splash" of silver nitrate). This mixture was ripened 5 min. at 105°F and then solution C added thereto over a 30 second period (second "splash" of silver nitrate). After ripening this mixture for 8 minutes, solution D was added to stop the ripening process. The coagulant was then added to coagulate the gelatino-silver halide as "curds" and these curds were then washed to remove excess soluble salts by adding deionized water and decanting to remove the water and salts. The G solution was available to adjust the pH to 3.0. For control purposes, a splash precipitation process identical to this one, but without any seeds present, was also run (Sample 5). Samples of the emulsion were then analyzed using the Particle Size Analyzer. Additionally, electron micrographs were taken of each emulsion. These results indicate that the final emulsion in each case had crystals of approximately the same volume as the control and, more importantly, that these emulsions were more uniform than the control. The control emulsion was not uniform and had a wider distribution of grain sizes.

Sample	Volume (μ^3)	σg*
1	0.291	1.86
2	1.456	1.50
3	0.258	1.56
4	0.505	1.37
5	0.373	2.11

* a polydispersity index-the smaller σg, the more uniform the range of particle sizes.

EXAMPLE 2

Four additional splash-prepared silver iodobromide emulsions were made. In three of these emulsions, seeds of 0.068 μ^3, $\sigma g=1.34$, silver iodobromide (2% iodide) were used in varying proportions. The procedures followed were identical to Example 1 except for the amount of the first silver splash (30% vs ca. 27% in Example 1) and the amount of seeds used which was as follows:

Sample	Amt. of Seed (moles/mole of $AgNO_3$)	Volume (μ^3)	σg
1	0.05	0.38	1.88
2	0.1	0.51	1.72
3	0.2	0.45	1.36
4	none - control	0.48	1.85

After the completion of the emulsion making process, by splash techniques, the particle sizes were examined and electron micrographs taken. Samples 2 and 3, the samples of this invention, exhibited improved uniformity and particle sizes close to that of the control emulsion. This example demonstrates that up to 0.2 moles of seeds/mole of $AgNO_3$ can be tolerated.

EXAMPLE 3

To demonstrate the photographic utility of emulsions prepared according to the teachings of this invention, four more splash-prepared emulsions were prepared as described in Example 1. The seeds used in three of these emulsions were identical to those of Example 2. The addition of the silver nitrate solution to the emulsions was varied as described below:

Sample	Type of Mix
1	Two-quick splashes, 30 seconds (same as EX. 1)
2	2 long splashes (4.8 and 4.9 minutes)
3	1 long splash (7.5 minutes)
4 - Control - No seeds	Two-quick splashes (same as EX. 1)

These emulsions were then brought to their optimum sensitivity with gold and sulfur sensitization as is well known to those skilled in the art. After the addition of the usual wetting agents, antifoggants, hardeners, etc. each emulsion was then coated on polyethylene terephthalate film supports suitably coated with a subbing layer and a thin anchoring substratum of gelatin. Each sample was overcoated with a hardened gelatin antiabrasion layer. Coating weights were about 47 mg $AgBr/dm^2$. Sample strips from each coating were sandwiched between two Cronex® HiPlus screens and exposed to an X-ray source operated at 60 Kvp, 100 ma at 40 inches for 40 milliseconds through a $\sqrt[2]{2}$ aluminum step wedge. They were then processed in a standard hydroquinone/phenidone mixed developer, followed by fixing and washing in a conventional manner. Sensitometry obtained was as follows:

Sample	Fog	Speed	TOE Gradient	TOP Density	$V(\mu\ )^3$	σg
1	0.16	41	2.44	1.84	0.44	1.27
2	0.15	36	2.37	2.07	0.43	1.28
3	0.15	32	2.17	1.98	0.36	1.49
4 Control	0.26	100	1.98	2.22	0.40	2.04

Electron micrographs indicate that the control emulsion had standard splash-prepared grains with a variety of grain sizes while those of the invention were more uniform and had particle sizes close to that of the control grains. One can see that the emulsions of this invention produced better gradients in the toe region then the control.

EXAMPLE 4

Four splash-prepared emulsions were made for this example as taught in Example 1. The three emulsions representing this invention used seed grains identical to those of Example 2 added at 0.2 mole/mole of added $AgNO_3$. Variations in the making procedures were as follows:

Silver halide composition AgIBr (4% iodide).
Added ammonia to A solution alone.
Iodide addition - 1/2 to A solution, 1/2 added after 1st silver nitrate splash.

The % silver in the first splash was varied as shown below. A Control (no seeds) was also employed. The emulsions were redispersed, sensitized, coated, overcoated, dried, exposed and processed as described in Example 3. The following results were obtained:

Sample	% Ag in 1st Splash	Fog	Speed	Gradient	Top Density	(μ^3) V	σg
1	25	0.18	52	2.52	1.80	.42	1.24
2	45	0.16	47	2.43	1.68	.43	1.29
3	65	0.16	47	2.59	1.80	.39	1.27
4 Control	-	0.18	100	2.16	2.13	.50	1.86

Other experiments were also conducted with variants in procedures such as lowered ripening times and lowered ripening temperatures. In all cases, the emulsions made according to this invention had high gradients but somewhat lower speeds. And, in all cases, the electron micrographs showed that the grains from the emulsions representing this invention had particle sizes close to that of the control grains and that the particle sizes were more uniform than the controls. These experiments, then, demonstrate the wide utility of the procedures of this invention.

EXAMPLE 5

To further demonstrate the utility of the process of this invention, two splash-prepared emulsions were made in the manner described in Example 1 except that seeds were added to one and the other (Control) prepared without seeds. The type of seeds and amount was as described in Example 2. During the precipitation process samples were withdrawn at regular intervals for analysis of particle size and examination by electron microscopy. These results indicate that the emulsion of this invention (seeded) ripened faster than the control and the grains reached their optimum size and size distribution sooner.

Time (minutes after beginning addition of 1st Ag solution) the second silver solution is added at 5 min.

	1	3	5	7	9	11	13
Seeded							
$V(\mu^3)$	0.14	0.17	0.19	0.40	0.45	0.46	0.47
σg	2.18	1.37	1.31	1.51	1.39	1.38	1.38
Control							
$V(\mu^3)$	0.014	0.15	0.14	0.21	0.33	0.39	0.41
σg	3.84	2.57	2.44	5.78	2.96	2.00	2.22

EXAMPLE 6

In a like manner two more splash-prepared emulsions were made following procedures previously described. In this case, the procedures were as described in Example 4, Sample 1 except that 1/2 I^- added to "A", 1/2 I^- added to mix vessel over 7 minutes beginning with the 1st silver splash. One emulsion had seeds; the other was the control. After ripening and redispersing the emulsion, the emulsions were sensitized. During these procedures, varying samples of the emulsions were sensitized at varying levels of sulfur sensitizer and varying digestion times. Sensitometric results indicate that the emulsions prepared according to the teachings of this invention have wider sensitization latitude than the control. Results were as follows:

Crystal parameters	Vol. (μ^3)	σg
Control	.32	2.16
Experimental	.30	1.56

Sensitization conditions:

1.3 mg $AuCl_3$/mole Ag; 0.1 g NaSCN/mole Ag for both;

for control, 1.7 mg/mole Ag }
} of $Na_2S_2O_3 \bullet 5H_2O$
for experimental, 2.7 mg/mole Ag }

typical stabilizers were added, samples coated

Exposure, development conditions:
Kodak Model 101 process and control sensitometer, 1/5 sec. exposure through $\sqrt[2]{2}$ stepwedge; developed in HSD at 84°F for 90 seconds.

Results:

Digestion Time (min.)	Fog	Rel. Speed	Top Density	Gradient	Coating Weight (mgAgBr/dm^2)
Control					
50	.16	50	1.75	1.07	49
60	.17	100	2.01	1.27	48
70	.72	100	2.09	0.85	46
80	1.39	60	2.30	0.48	50
Experimental					
60	.23	100	1.88	1.43	47
70	.29	100	1.87	1.30	49
80	.33	84	1.86	1.20	47
90	.45	84	1.80	1.04	48

Besides showing better digestion latitude, the product shows equivalent speed with higher gradient.

EXAMPLE 7

A direct positive emulsion was made from silver iodobromide precipitated by splash procedures in the presence of Ag(I)Br seed crystals. Three emulsions were made. One, the control, had no seeds; number two had seeds of 0.0086μ^3 present; and number three had seeds of 0.0378μ^3. These emulsions were redispersed in gelatin, fogged with tetraazaundecane, and the usual wetting agents, antifoggants and coating aids added thereto. Each emulsion was coated on a support as previously described and strips from the coatings were exposed with an EG and G sensitometer to a tungsten flash for 10^{-2} seconds. These strips were then developed in DP-2 for 90 seconds followed by fixing, washing and drying. Sensitometric results show that speed equivalent to the control with higher gradients was obtained.

EXAMPLE 8

An emulsion was made following splash techniques. First, a seed emulsion was generated in situ using BDJ techniques. The process was as follows:

- preparation of monodisperse AgIBrCl (ca. 0.5% I, 18.8% Br and 80.7% Cl).

  The first 50% of the volume is a monodisperse BDJ mix at 120°F, pAg 6.17 with:

  a) 0-1.7% - single jet addition of 3N $AgNO_3$ to seed.

  b) 1.7-37.5% - BDJ precipitation with 1.3% I^-, 52% Br^-, 46.7% Cl^- and enough rhodium chloride for 0.2µ M/unit of silver nitrate as rhodium.

  c) 37.5-50% - BDJ precipitation with 100% Cl.

At this point analysis by Particle Size Analyzer showed crystals with $V = 0.0056\mu^3$ and $\sigma g=1.40$.

Next, the temperature was reduced to 110°F and KCl was added rapidly (1.4 X the amount of $AgNO_3$ remaining to be added). The temperature dropped to 100°F and pAg was 9.96. After 1 minute,

$AgNO_3$ (remaining 50% of volume) was added and the resulting emulsion stirred 5 minutes. The temperature was 108°F after the $AgNO_3$ addition and dropped to 104°F after 5 min. The pAg was 7.65.

This final emulsion was analyzed by Particle Size Analyzer and found to contain crystals with $V=0.0150\mu^3$ and $\sigma g=1.55$.

EXAMPLE 9

A sample of BDJ prepared seeds (AgIBr, 2.5% I^- - with a grain size of ca. $0.0378\mu^3$) was placed in a mixing kettle and sufficient potassium iodide added to convert the entire sample to AgI. A splash-precipitation process (see Example 1) was then run on these seeds. Films made from this emulsion, after sensitization and coating as previously described, were processed with equivalent sensitometric results. The grains were analyzed and found to be uniform in size and shape.

	Fog	Rel. Speed	Gradient	Top Density
Experiment	.14	31	3.8	3.7
Control	.15	100	3.5	3.8

EXAMPLE 10

A sample of BDJ prepared seeds (Ag 1.5% I^- 98.5% Br^-, with a grain size of $0.04\mu^3$) was prepared. Solutions for splash preparation of AgIBr (2% I^-) were made up as follows:

A. Solution ("Heel", made up in preparation vessel):

Distilled water - 955 cc

NH_4Br solid - 310 g

0.5N KI - 120 cc

Gelatin - 40 g

Seeds - (0.2 moles/mole of $AgNO_3$).

Hold at 40.6°C

B. Solution (1st Silver):

Distilled water - 1020 cc

Solution of Thallium Nitrate (8 g/liter) in water - 5.4 cc

3N $AgNO_3$ - 320 cc

Hold at 29.8°C

C. Solution (2nd Silver):

Distilled water - 373 cc

3N $AgNO_3$ - 680 cc

Thallium Nitrate (see above) - 4.4 cc

Hold at 12°C

Procedure:

- 5 min. before 1st silver, add seeds to A solution.
- 1 min. before 1st silver, add 191 cc of 12M NH_4OH to B solution.
- At time = 0, add B to A in 30 seconds.
- At time = 3 min. add C to A in 15 seconds.
- At time = 9 min., stop ripening with 124 cc glacial acetic acid
- Coagulation and wash procedures as described in Example 1.

The emulsion prepared in this manner was then redispersed in gelatin, sensitized with gold and sulfur, wetting agents, antifoggants, etc. added, and coated and overcoated as previously described. For control purposes, an element was made, sensitized, and coated under the same conditions but without the addition of the seed crystals of silver halide. Samples from the coatings were exposed, developed fixed, washed and dried as previously explained with the following sensitometry:

Sample	Emul. Grain Size (μ^3)	Fog	Rel. Speed	Avg. Gradient	Top Density	σg
Control	0.23	.22	100	2.86	2.09	2.3
Of the Invention	0.20	.13	66	3.48	2.30	2.1

One can see that the film prepared from the emulsion made following the teachings of this invention had excellent gradient and top density, though somewhat lower speed than the control. The grains, when examined under an electron microscope, were uniform in size and shape.

EXAMPLE 11

Following the procedures of Example 1 two additional splash-prepared emulsions were made varying the size of the seed emulsion or grains used. In one case, the BDJ prepared seeds were AgIBr seeds of about $0.06\mu^3$ (ca. 2.5% I^-) and in the second case were AgIBr seeds of about $0.039\mu^3$ (ca 2.5%I^-). The emulsions were analyzed by particle size analyzer and by electron micrograph and found to contain uniform particle sizes, indicating that one can use fairly large seed grains within the ambit of this invention.

Seed Vol. (μ^3)	Final Crystal Vol. (μ^3)	σg
0.039	0.24	1.48
0.06	0.44	1.27

EXAMPLES 12 and 13

In a like manner, additional splash-prepared emulsions were made using BDJ-prepared seeds of AgIBr (ca. 2.5%I^-) and additionally containing small amounts of rhodium (EX. 12) or lead (EX. 13). The process of preparing these seed grains is well known and is fully described in U.S. Pat. 4,221,863 (Overman, Sheeto). These splash-prepared emulsions were redispersed and then fogged to obtain excellent quality direct positive elements with good uniformity of grain.

EXAMPLE 14

Two mixes: control, normal splash mix; Experimental (seeded), made as in Example 4, Sample 1, except that 1/2 I^- added to "A" solution, 1/2 I^- added over 7 min. beginning with addition of 1st silver solution.

Sensitization: 1.37 mg/Ag mole $AuCl_3$ } for both
0.11 g/Ag mole NaSCN }

for control: 1.66 mg $Na_2S_2O_3 \bullet 5H_2O$/Ag mole
for experimental: 2.66 mg $Na_2S_2O_3 \bullet 5H_2O$/Ag mole

Control digested: 50 min
Experimental: 70 min

Results, after exposure and development as in Ex. 6:

	Vol. (μ^3)	σg	Fog	Speed	Gradient	Top Density
Control	0.27	2.00	0.24	100	1.02	1.86
Experimental	0.32	1.76	0.17	104	1.21	1.89

This result shows higher gradient and slightly higher speed for the emulsion made according to the teachings of this invention compared to that of the control emulsion.

CLAIMS

1. A process for preparing silver halide emulsions with a narrow grain size distribution, wherein silver nitrate is added by a splash method to an aqueous solution containing (a) one or more alkali halides in a protective colloid and (b) monodisperse silver halide seed crystals.

2. The process of claim 1 wherein the monodisperse seed crystals (b) are prepared by a balanced double jet process.

3. The process of claim 1 wherein a portion of the alkali metal halide is added initially, and the remainder is added after part of the silver nitrate has been added.

4. A gelatino-silver halide emulsion produced by the process of claim 1.