

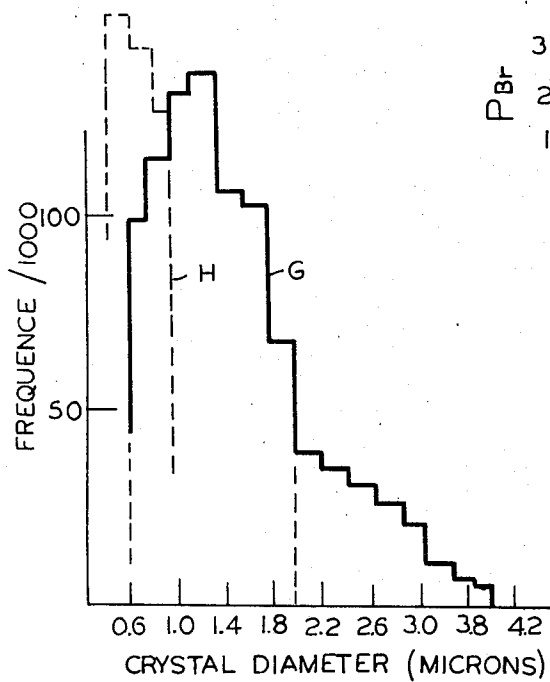
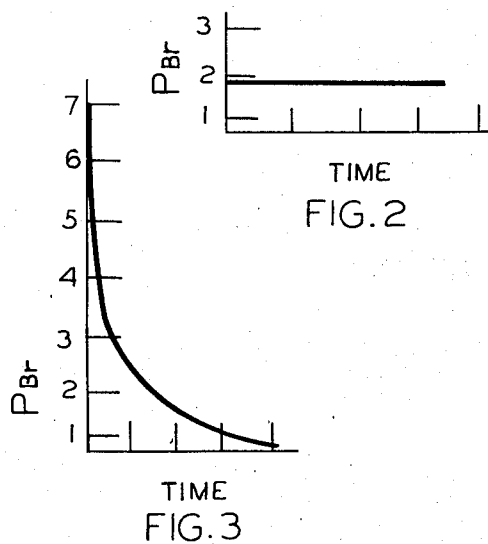
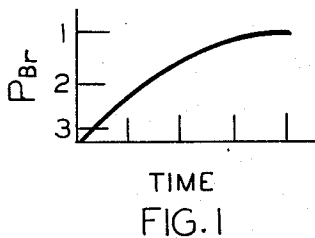
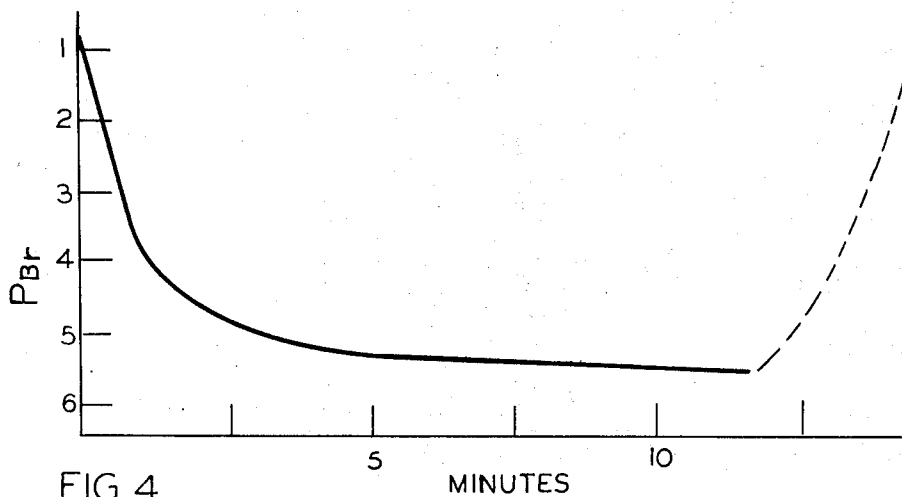
Aug. 10, 1971

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3,598,593

PHOTOGRAPHIC EMULSIONS AND METHOD OF MAKING

Filed Dec. 21, 1965



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3,598,593

PHOTOGRAPHIC EMULSIONS AND METHOD OF MAKING

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Filed Dec. 21, 1965, Ser. No. 515,391
Int. Cl. G03c 1/02

U.S. Cl. 96—94

8 Claims

ABSTRACT OF THE DISCLOSURE

Preparation of gelatin-silver bromide photographic emulsions, involving precipitation of the silver bromide by admixture of aqueous solutions of a water soluble silver salt and a water soluble bromide, wherein the pBr is maintained above 5 during formation of the major portion of the silver bromide, whereby the average particle size of the silver bromide forming is above 0.8 micron, and finally adding excess bromide solution at the end of the silver bromide formation.

The present invention relates to photographic emulsions and to a method of making the same. It has particular application to the making of silver halide emulsions wherein the grain size of the silver halide particles is carefully controlled. In general, it is applicable more especially to ammonia type emulsions, although not necessarily limited thereto.

In the prior art, emulsions of this general type are usually made either by addition of an ammoniacal silver nitrate solution to a solution of alkali halides and gelatin, or by the simultaneous and controlled rate addition of an ammoniacal silver nitrate solution and of a solution of alkali halides to a gelatin solution. The scheme first mentioned is commonly referred to as the single jet addition method. The second scheme is commonly referred to as double jet addition, wherein the two main silver halide forming ingredients are added simultaneously. The same general procedures may be applied to emulsions which do not involve ammonia but, generally speaking, ammonia is employed in making such emulsions and is preferred.

In the past it has generally been believed that it is quite essential in either the single jet or the double jet type of emulsion formation to maintain always a substantial excess of halide ions. Otherwise, it has been feared that the emulsion might show high fog levels. In fact, in many cases, high fog levels have resulted from other methods of preparation.

According to the present invention, however, it has been found that it is not necessarily true that high fog levels will result if there is not a substantial excess of halide ions maintained. As a matter of fact, it is found that with proper control of ion concentrations, ammonium emulsions may be made successfully even though during the crystal formation there is no excess of halide ions at any time or even when there is, for a time at least, a slight excess of silver ions, one can still obtain good emulsions of low fog level. Also, it has been found further that by a careful and continuous control of the concentration of the respective ions, photographic emulsions having very interesting properties, and sometimes very desirable properties, may be obtained. The crystal growth and the eventual crystal size of the silver halide particles, in particular, may be controlled quite well and a superior product may be obtained in this manner.

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In the general case of ammonia emulsions, the ammonia can either be added with the silver nitrate solution or it may be added after mixing the silver nitrate and part or all of the halide solution.

According to further aspects of the present invention, after it was found that it is not essential to maintain a substantial excess of halide ions, a more detailed investigation on correlation of crystal growth and ion concentrations in the photographic emulsions was undertaken. As a result of this investigation it was further found that it is possible to use only a very small excess of halide ions and still obtain excellent products. It was also found that even a small excess of silver ions could be employed during the crystal silver halide grain formation. With proper control, neither of these procedures causes emulsion fog. Furthermore, the growth of the silver halide crystals to larger grain sizes, on the average, and of greater uniformity, is enhanced. The new process permits preparation of silver halide crystals with an average size above about 1.5 microns and also with a narrow crystal size distribution. In the prior art, by analogous procedures, the average size was smaller and size distribution was wider. Moreover, the emulsions so prepared may be made under much milder conditions than has been considered possible with conventional prior art procedures.

A further advantage resulting from the invention is that optical sensitization of the emulsion crystals seems to be facilitated, as compared with conventional emulsions, using the new technique.

It has also been found that by holding the halide ion concentration constant during crystal formation the growth of crystals is definitely inhibited. As a matter of fact, the crystals will grow only to a limited size when a fairly narrow distribution of crystal sizes is to be maintained. Ordinarily, the largest average crystal size which may be obtained in this manner is about 0.8 micron diameter.

In the past, several procedures have been used in preparing single jet photographic emulsions. Generally, the total halide ions are placed in the vessel prior to addition of silver. This meant that the halide ion concentration in solution in the preparation vessel was very high as silver addition was started. As silver nitrate was added, the halide ion concentration, of course, dropped continuously, usually following a log *e* function.

On the other hand, when the double jet addition procedure of the prior art is followed the halide concentration in the solution may be controlled in various ways. Thus, it can either be kept constant during the entire addition period or it can be changed continuously. It may start high and drop to a lower level or it may start low and keep building up as the procedure continues, depending on the relative addition rates of silver and halide. Thus, somewhat as in the case of single jet addition, the halide ion concentration may be high at the beginning and decrease continuously or, alternatively, the silver ion concentration may be very high at the beginning of the making and gradually decrease towards the end of the addition of the two main reactants.

The scheme just mentioned, of starting off with a high silver ion concentration which gradually decreases toward the end of the addition, apparently has attracted little attention in the past, probably because of the fear that such emulsions would show unduly high fog density. According to the present invention, however, it has been found, as suggested above, that emulsions prepared according to this scheme do not necessarily possess high fog

densities but under proper control, can be made to possess very interesting properties, making them useful for some practical purposes.

The invention will be more fully understood by reference to the attached drawing and the detailed specification which follows wherein examples are set forth. Referring first to the drawing:

FIG. 1 shows a system starting with low halide ion concentration which boulds up as the work proceeds.

FIG. 2 shows graphically the maintenance of a constant halide ion concentration in a double jet addition process.

FIG. 3 shows a system of double jet addition having silver ion excess at the start.

FIG. 4 shows graphically a scheme of ion concentration control which is particularly suitable for the present invention wherein the halide ion concentration starts off high, drops gradually and more or less exponentially, being built up at the end of the mixing procedure to the desired level.

FIG. 5 shows graphically the distribution of grain sizes obtained by a preferred procedure.

In preparing for the examples which are detailed below ammonia emulsions were made, using two different techniques. In the first of these, the silver halide was formed in complete absence of ammonia, the ammonia being added later, at the beginning of the digesting. In the second procedure, the ammonia was added earlier, being present during the formation of the silver halide, preferably being added together with the silver nitrate solution. The halide ion concentration was varied according to FIGS. 2 and 3, respectively, for the emulsions prepared according to each of the procedures mentioned above. The addition of the silver nitrate and of the halide salt solution was automatically timed and was kept under strict control throughout the entire addition period. It followed the procedure indicated in FIG. 4 which shows the ion concentration of halide versus time throughout the preparation period. The results also are tabulated below.

Crystal size distribution data for both types of emulsions are given by the solid graph line G of FIG. 5 and are tabulated below. The formulations for the actual examples are as follows:

EXAMPLE A-2

- Receiving vessel:
 - Water—2260 ml.
 - KBr (1.0%)—2.6 ml.
 - Gelatin—120 g.
- Salt solution:
 - Water to make 1400 ml.
 - Ammonium bromide—383.8 g.
- Silver nitrate solution:
 - Water to make 2800 ml.
 - Silver nitrate—640 g.

The salt solution and the silver nitrate solution were added simultaneously to the solution in the receiving vessel at 48° C. The addition required 12 minutes, following the addition scheme when uniform halide in concentration was maintained as in FIG. 2. At completion of the addition, 320 ml. of aqueous ammonia solution (28%) were added in one portion. Digesting was carried out for 90 minutes. Thereafter the emulsion was precipitated, washed and reconstituted.

EXAMPLE A-3

- Receiving vessel:
 - H₂O—2260 ml.
 - KBr (1.0%)—2.6 ml.
 - Gelatin—120 g.
- Salt solution:
 - Water to make 1400 ml.
 - Ammonium bromide—369 g.
- Silver nitrate solution:
 - Water to make 2800 ml.
 - Silver nitrate—640 g.

The salt solution and the silver nitrate solution were added simultaneously in this case to the solution in the receiving

vessel at a temperature of 48° C. The addition scheme of FIG. 4 was followed, the ion concentration being controlled by adjustment of both jets. When all the silver nitrate solution was added, the remaining salt solution was added slowly to bring the pBr back to the starting level, covering a period of about 2 minutes. 320 ml. of ammonia solution (28%) were added last and the mixture was digested for 90 minutes. Thereafter, the emulsion was precipitated, washed and reconstituted.

The products of the emulsions were analyzed by electron microscopy. The size of the silver grains and their relative proportions are indicated in the table below. It will be noted that the great bulk of the grain sizes were between 0.8 and 2.0 microns in diameter.

TABLE I

$\overline{X}$ (μ)	s (μ)	V (percent)	M (μ)	i (μ)
1.62512	.80534	49.55580	1.41168	.2000
SK _p	β_1	β_2	$\overline{X}$ (μ)	Y _o
.79507	1.59666	4.11891	1.62512	99.07389
Measured dia. (cm.)	f	f ₁₀₀₀	Midpoint (μ)	Y _o
.6				
.8	4,032.1	100.15	.7000	51.21
1.0	4,718.0	117.19	.9000	66.05
1.2	5,472.7	135.94	1.1000	80.10
1.4	5,949.5	140.33	1.3000	91.32
1.6	4,386.8	108.96	1.5000	97.88
1.8	4,135.6	102.72	1.7000	98.64
2.0	2,585.4	64.22	1.9000	93.46
2.2	1,570.7	39.01	2.1000	83.26
2.4	1,374.5	34.14	2.3000	69.73
2.6	1,222.6	30.37	2.5000	54.91
2.8	1,044.7	25.95	2.7000	40.65
3.0	868.5	21.45	2.9000	28.30
3.2	689.6	17.13	3.1000	18.52
3.4	315.3	7.83	3.3000	11.39
3.6	261.7	6.50	3.5000	6.59
3.8	66.1	1.64	3.7000	3.58
4.0	1,868.3	46.40	3.9000	1.83
40,257.8		1,000.00		

By comparison with the crystal size distribution obtained by conventional methods, it will be noted that the average grain size of the silver halide indicated by the solid line G, FIG. 5, was much greater than that of the conventional method indicated by the dotted line H of the same figure. In the latter case, the average grain size was about 0.8, whereas the average for the improved product was slightly over 1.5 microns. At the same time, the great bulk of the grains obtained by the new procedure were within the relatively narrow grain size of 0.6 to 2.0 microns average diameter.

It will be noted, particularly from FIG. 5 and the data in Table I, that the average grain size of the emulsion, prepared according to the scheme of FIG. 4, is considerably greater than 0.8 micron, substantially greater than 1.0 micron, and in fact is above 1.5 microns. At the same time, crystals or grains of excessively large size are avoided, less than 10% being above 3.0 microns. Such emulsions have excellent sensitization properties for many purposes.

It will be noted, also, that the halide ion concentration can be quite low during much of the silver halide formation time. As long as it is raised at the end of such time, to prevent fogging in storage, etc., the system appears to be very satisfactory.

It will be obvious that modifications may be made in the process and it is intended by the claims which follow to cover such modifications as would suggest themselves to those skilled in the art, as far as the prior art properly permits.

What is claimed is:

1. In the preparation of a silver halide-gelatin photographic emulsion, the improvement which comprises precipitating silver bromide having a grain size substantially in excess of 0.8 micron average diameter by simultaneous addition of aqueous solutions respectively of a water soluble silver salt and a water soluble bromide to an aqueous gelatin solution at such rates wherein the

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bromide concentration is initially at a pBr below 1, is then lowered to a level above pBr 5 during formation of the major portion of the silver bromide and increasing the bromide concentration at the end of said formation, preparatory to washing and reconstitution.

2. A photographic emulsion containing silver bromide precipitated by admixture of aqueous solutions of a water soluble silver salt and a water soluble bromide with aqueous gelatin at such rates that the bromide concentration is initially at a pBr below 1, is then lowered to a level above pBr 5 during formation of the major portion of the silver bromide and increasing the bromide concentration at the end of said formation, said grains having an average diameter in excess of 1 micron.

3. A method as defined in claim 1 wherein the silver salt is added in at least stoichiometric amount relative to the added bromide during the formation of most of the silver bromide.

4. A method as defined in claim 1 wherein the silver salt is silver nitrate and ammonia is added after completion of the precipitation of the silver bromide.

5. A method as defined in claim 1 wherein the silver salt is ammoniacal silver nitrate.

6. A method as defined in claim 1 wherein the average

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grain size of the precipitated silver bromide is greater than 1.0 micron.

7. A method as defined in claim 1 wherein the average grain size of the precipitated silver bromide is more than 1.5 microns.

8. A photographic emulsion according to claim 2 wherein the average grain size of the silver bromide exceeds 1.5 micron and 90% of the grains have an average grain size below 3 microns in diameter.

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