

UNITED STATES PATENT OFFICE

2,592,250

PHOTOGRAPHIC SILVER BROMIDE EMULSION CONTAINING SOME SILVER IODIDE

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No Drawing. Application March 22, 1949, Serial
No. 82,914. In Great Britain May 13, 1947

2 Claims. (Cl. 95—7)

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This invention relates to sensitive photographic silver halide emulsions.

This invention relates to photographic emulsions which are capable of forming an internal latent image upon exposure to light. The emulsions which form an internal latent image are known (Mees, "The Theory of the Photographic Process" (1942), page 166; Berg, Marriage and Stevens "Journal Optical Society of America," vol. 31 (1941), page 385). In Knott and Stevens, U. S. application Serial No. 528,738, filed March 30, 1944, now abandoned, continuation-in-part application Serial No. 756,636 now U. S. Patent 2,456,956, a process is described employing this type of emulsion which is designated therein as type I. The emulsion of the present invention is useful in the process of the Knott and Stevens application.

Photographic emulsions are usually made by the following series of operations: (1) emulsification or digestion or ripening of the silver halide, (2) freeing the emulsion from excess soluble salts usually by washing, (3) the second digestion or after-ripening step. Silver nitrate or other soluble silver salt solution is added to a solution of the halide in the presence of a small amount of gelatin. The silver halide produced in this way is usually silver bromide containing a small amount of iodide. Gelatin is added to the emulsion during or before the second digestion and the content of the sensitizers, usually sulfur compounds, normally present in the gelatin acts to increase the sensitivity of the final emulsions.

Photographic emulsions may be either neutral or ammoniacal emulsions. Ammonia is ordinarily used during emulsification but if a neutral emulsion is being prepared, no ammonia is used there and temperatures in the neighborhood of 70–90° C. are used in the precipitation of the silver halide.

Since the precipitation of the silver halide is carried out with an excess of soluble halide, it is necessary to wash the excess soluble halide and other soluble salts from the emulsion after emulsification and digestion. This operation removes the potassium nitrate and any excess of potassium bromide or other soluble halide present in the emulsion. The emulsion is then subjected to the second digestion or after-ripening during which the sensitivity continues to increase. The emulsion may then be coated or stored for future coating.

According to the present invention, there is provided a method of making a sensitive photographic silver halide emulsion which comprises first forming in the presence of inert gelatin, and in one or more stages, an emulsion of silver salt grains consisting at least partly of a silver salt which is more soluble in water than is silver

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bromide, subsequently converting the whole of such grains to silver bromide or iodobromide and preferably if the silver iodide content of the emulsion is less than 6% of the total amount of silver halide, treating such grains with an iodine compound to bring the silver iodide content up to at least 6%, ripening the emulsion and then either washing out some of the soluble salts or washing out the whole of the soluble salts followed by addition of soluble salts such as soluble chloride or bromide.

The soluble halide content of the finished emulsion should be above 0.03 gram of potassium bromide per liter (preferably between 0.03 and 0.3 gram per liter) or the equivalent of any other bromide or chloride or mixture thereof. The term "equivalent" as used here means that there is the same suppressing action on the silver ion concentration of the emulsion. For instance, if potassium chloride alone is used as the soluble halide, the concentration should be more than about 0.4 gram per liter of emulsion.

It is noted that photographic gelatin contains impurities which may or may not be desirable in a photographic emulsion. For example, gelatin contains sensitizers, mostly sulfur compounds, which are ordinarily useful in photographic gelatin. Such compounds are, however, undesirable in the gelatin used according to our invention and our process requires the use of inert gelatin, that is, gelatin from which sulfur compounds or compounds which have labile sulfur atoms have been removed (Steigmann, "Journal Society Chemical Industry," vol. 61, 1942, page 162).

It is also desirable to avoid digestion, that is, treatments after washing which increase sensitivity such as heat treatment. Some ripening may be performed before the addition of iodide in those cases where such addition is necessary. Preferably the iodide content of the final emulsion should be at least 10 to 20%. Our emulsions are made in the following general way.

The first step is to form in the presence of a small amount of inert gelatin a silver salt which is more soluble in water than silver bromide, that is, silver chloride or silver thiocyanate. This is accomplished by adding separate solutions of potassium chloride in water, and silver nitrate in water, to a solution of gelatin containing a small amount of potassium chloride. These solutions are added slowly and the emulsion thus formed is ripened for about 1 minute.

The next step in our process is to convert the silver chloride or other silver salt more soluble in water than silver bromide, to a silver halide less soluble in water than silver chloride, that is, silver bromide, silver iodide or silver iodobromide. This is accomplished by adding to the silver chloride emulsion a solution of an excess of potassium

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bromide or a mixture of potassium bromide and potassium iodide or other soluble bromide or iodide. The silver iodide content of the emulsion should preferably be at least 6% of the total amount of silver halide and if the iodide content is less than 6%, it can be brought up to at least 6% by treating the emulsion with an iodine compound such as potassium iodide. It is preferable to bring the iodide content to at least 10 to 20% of the total halide content of the emulsion.

The next step in our process is to add additional gelatin and ripen the emulsion for about 15 minutes at a low temperature.

The final step is the washing to remove a portion of the soluble salts. A distinction over the usual emulsion making procedure is that a portion of the soluble salts are left in the emulsion. Either some of the soluble salts may be removed by washing or the whole of the soluble salts may be removed followed by addition of the required amount of soluble salts such as soluble chloride or bromide. During all of the emulsion-making procedure, the temperature of the solutions and emulsions should not be above about 50° C. An example of an emulsion made according to the present invention is as follows:

Example I

Solution No. 1:			
Inert gelatin	gms.	102.6	} at 40° C.
KCl	gms.	102.6	
Water	ccs.	2873	
Solution No. 2:			
KCl	gms.	513	} at 45° C.
Water	ccs.	2668	
Solution No. 3:			
AgNO ₃	gms.	1000	} at 45° C.
Water	ccs.	2668	
Solution No. 4:			
KBr	gms.	820.8	} at 45° C.
KI	gms.	205.2	
Water	ccs.	2565	

Run Solutions Nos. 2 and 3 simultaneously into Solution No. 1 in a vessel, taking 90 seconds to do this. Then ripen for 1 minute at 45° C. Next add Solution No. 4 then ripen for 20 minutes at 45° C. Next add 1206 gms. of inert gelatin (dry). Then ripen at 45° C. for 15 minutes during which time the gelatin dissolves. Set and shred the emulsion and then wash until free from all soluble bromide and then add about 770 ccs. of 10% solution of KCl (by weight), and then add water to make 18 litres.

Example II

Solution No. 1:			
Inert gelatin	gms	128	} at 45° C.
KCl	gms	10.2	
Water	ccs	2873	
Solution No. 2:			
KCl	gms	513	} at 45° C.
Water	ccs	2668	
Solution No. 3:			
AgNO ₃	gms	1000	} at 45° C.
Water	ccs	2668	
Solution No. 4:			
KBr	gms	61.6	} at 45° C.
KCl	gms	20.5	
KI	gms	51.3	
Water	ccs	257	
Solution No. 5:			
KBr	gms	770	} at 45° C.
KI	gms	154	
Water	ccs	1796	

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Run Solutions Nos. 2 and 3 simultaneously into Solution No. 1 in a vessel, taking 90 seconds to do this. Then ripen for 30 seconds at 45° C. Next add Solution No. 4 taking 2 minutes to do this and ripen for 15 minutes at 45° C. Next add Solution No. 5 taking 25 minutes to do this, and ripen for 1 minute at 45° C. Then add 51.3 ccs. of ammonia (S. G. 0.935) and 1180 gms. of dry inert gelatin at 45° C. and ripen for 15 minutes at 45° C. during which time the gelatin dissolves. Set, wash and shred, add 770 ccs. of 10% solution of KCl, and then add water to make 18 litres.

It will be understood that the examples and modifications included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

This application is a continuation-in-part of our application Serial No. 790,232, filed December 6, 1947, now abandoned.

We claim:

1. The method of making a sensitive silver halide emulsion which comprises the addition of aqueous silver nitrate solution to at least an equivalent amount of aqueous alkali chloride solution and gelatin, which alkali chloride reacts substantially completely with all of the silver to form silver chloride, then adding an aqueous mixture of alkali bromide and iodide in an amount which will completely convert substantially all of the silver chloride to silver bromide and silver iodide so that the resulting emulsion will contain at least approximately 6 per cent silver iodide, the remainder being essentially all silver bromide, ripening the emulsion, and washing out at least some of the soluble salts and bringing the soluble halide content of the emulsion to a potassium bromide equivalent concentration above 0.03 gram per liter, all of the operation being conducted at less than about 50° C.

2. The method of making a sensitive silver halide emulsion which comprises the addition of aqueous silver nitrate solution to at least an equivalent amount of aqueous potassium chloride solution and gelatin, which potassium chloride reacts completely with all of the silver to form silver chloride, then adding an aqueous mixture of potassium bromide and iodide in an amount which will completely convert substantially all of the silver chloride to silver bromide and silver iodide so that the resulting emulsion will contain approximately 6 per cent silver iodide, the remainder being silver bromide, ripening the emulsion, and washing the emulsion to bring the soluble halide content to a potassium bromide equivalent concentration above 0.03 gram per litre, all of the operations being conducted at less than about 50° C.

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REFERENCES CITED

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