

(19)



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(11) Publication number:

**0 600 543 A1**

(12)

**EUROPEAN PATENT APPLICATION**(21) Application number: **93203293.1**(51) Int. Cl.<sup>5</sup>: **G03C 1/047, G03C 1/015**(22) Date of filing: **25.11.93**(30) Priority: **28.11.92 GB 9224967**(43) Date of publication of application:  
**08.06.94 Bulletin 94/23**(84) Designated Contracting States:  
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**Harrow Middlesex HA1 4TY (GB)**(54) **Process for producing silver halide grains.**

(57) A process for the production of silver halide grains in which an aqueous solution comprising a water-soluble halide, a water-soluble silver salt and a protective colloid is produced in a reactor and silver halide grains are formed in the reactor by reaction of the halide and the silver salt, nucleus formation and crystal growth both taking place in the reactor characterised in that a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000 daltons.

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This invention relates to a process for producing silver halide grains and to a process for the formation of a photographic emulsion.

The formation of silver halide grains has two main steps, these being (a) nucleus formation and (b) crystal growth. Nucleus formation (a) is a step in which new crystals are formed and a sharp increase in the number of crystals takes place. Crystal growth is a step in which new layers are added to existing crystals. Nucleus formation is rapid, generally taking less than a minute. Crystal growth is slower, generally taking 20 to 60 minutes.

In the formation of photographic emulsions silver halide grains are precipitated in the presence of a protective colloid i.e. gelatin. Conventional gelatin solutions display a sol-gel property and this generally constrains precipitation of silver halide emulsions in which gelatin is used as a peptizing agent to temperatures above 35 C.

Research Disclosure No 28453 (December 1987) mentions that fish gelatin solutions remain liquid at temperatures down to 10 C enabling silver halide precipitation to take place at temperatures which are lower than usual. However, fish gelatins can contain high levels of sulphur-containing impurities and in general are not to be recommended for the purpose of silver halide emulsion preparation.

European Patent Application EP-A-374853 relates to a process of producing silver halide grains in which the inventive step is to separate nucleus formation step (a) from crystal growth step (b) by carrying out the former in a separate mixer outside the reactor in which (b) takes place. The stated aim of this process is to produce silver crystal grains having a homogeneous halide composition in each crystal and having no halide distribution among the grains. The nucleus formation step in this process is carried out at a reduced temperature in the presence of low molecular weight gelatin which can be obtained from ordinary gelatin. However the use of low molecular weight gelatin in this process is confined to step (a) in the mixer. It is not used in step (b) in the main reactor.

According to the present invention we provide a process for the production of silver halide grains in which an aqueous solution comprising a water-soluble halide, a water-soluble silver salt and a protective colloid is produced in a reactor and silver halide grains are formed in the reactor by reaction of the halide and the silver salt, nucleus formation and crystal growth both taking place in the reactor characterised in that a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000 daltons.

Further according to the present invention we provide a process for the formation of a photo-

graphic emulsion in which an aqueous solution comprising a water-soluble halide, a water-soluble silver salt and a protective colloid is produced in a reactor and silver halide grains are formed in the reactor by reaction of the halide and the silver salt, nucleus formation and crystal growth both taking place in the reactor characterised in that a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000 daltons.

The silver halide grains are produced by reacting an aqueous silver salt solution and an aqueous halide solution in an aqueous colloid solution in the reactor. This can be done in any suitable manner. Possible modes of operation include the single jet method and the double jet method. In the single jet method the aqueous solution of the colloid and the halide are placed in the reactor and the aqueous silver salt solution is added with stirring for a suitable time. In the double jet method, which is preferred, the aqueous colloid solution is placed in the reactor and the aqueous halide solution and the aqueous salt solution are added to the solution in the reactor.

The modified mammalian gelatin has a mean molecular weight in the range 5000 to 30000, preferably in the range 10000 to 20000. Such modified gelatin can be obtained in a variety of ways. It can be obtained by treating an aqueous solution of normal gelatin, which generally will have a mean molecular weight of approximately 100000, with a gelatin decomposing enzyme such as trypsin. Alternatively the gelatin can be hydrolised with an acid, heating it at a low pH e.g. in the range 1 to 3, or with a base, heating it at a high pH e.g. in the range 10 to 12.

Suitably the process is carried out at a temperature up to 35 C, a preferred range being 5 to 35 C. In particular ambient temperature, i. e. the range 18 to 20 C, is very suitable for operation of the process. Heating of the reactor is preferably avoided. The process temperature is preferably controlled within a narrow range, i.e. to within 0.5 degrees and particularly to within the range 0.25 to 0.3 degrees C. Halides and silver salts are preferred which can be used to precipitate silver chloride, bromide, bromiodide or chlorobromide. Particularly preferred as the halide is sodium chloride and as the silver salt silver nitrate. If the halide and the silver salt are supplied to the reactor in the double jet method, it is convenient for them to be supplied at the same or at similar rates, suitable rates depending partly upon the scale of operation. It is preferred that during the process the vAg of the solution is controlled to prevent significant variation. By varying the process conditions silver halide grains and emulsions having different properties can be obtained. Amongst the emulsions that

can be obtained are chloride emulsions of cubic morphology with edge lengths in the range 0.05 to 0.2 microm.

The advantages of the invention, such as the precipitation of emulsions of small grain size, or less disperse grain size distribution, come largely from the reduction in silver halide solubility which is seen at low temperatures. Nucleation at low temperatures by the process of the invention could lead to emulsions having morphologies and/or sizes unobtainable in other ways. It may also be possible to obtain core shell or banded structures having more discrete separation between layers of different composition.

The invention is illustrated by the accompanying Examples:

#### EXAMPLE 1

2000 mls of an 8% solution of acid hydrolysed gelatin (molecular weight 20000 daltons) was placed in a kettle (reactor) and made up to 4.25 litres total using demineralised water. The temperature was reduced to 20 C, and the vAg adjusted to + 120 mV using sodium chloride solution. Chilled 3.0 molar solutions of silver nitrate and sodium chloride were then added over 20 minutes. The rate of addition was linearly increased from a starting rate of 20 mls/min to a final rate of 180 mls/min over this period, controlling the vAg throughout at + 120 mV. At this point a sample was taken for electron microscopy. An emulsion of cubic morphology was obtained, with an edge length of 0.12 microm.

#### EXAMPLE 2

2000 mls of an 8% solution of acid hydrolysed gelatin (molecular weight 20000 daltons) was added to a kettle (reactor) and made up to a total of 4.0 litres with demineralised water. The temperature was reduced to 20 C and the vAg adjusted to + 120 mV using a solution of sodium chloride. Chilled 3.0 molar solutions of silver nitrate and sodium chloride were then run into the kettle at 200 mls/min over a period of 5 minutes, controlling the vAg at + 120 mV throughout the run. At the end of the run a sample of the emulsion was removed for electron microscopy. An emulsion of cubic morphology and edge length 0.055 microm was obtained.

#### Claims

1. A process for the production of silver halide grains in which an aqueous solution comprising a water-soluble halide, a water-soluble silver salt and a protective colloid is produced in

a reactor and silver halide grains are formed in the reactor by reaction of the halide and the silver salt, nucleus formation and crystal growth both taking place in the reactor characterised in that a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000 daltons.

2. A process according to claim 1 characterised in that the mammalian gelatin has a mean molecular weight in the range 10000 to 20000 daltons.

3. A process according to claim 1 or claim 2 characterised in that the mammalian gelatin has been obtained by treating normal gelatin with the gelatin decomposing enzyme trypsin or by heating normal gelatin either at a low pH in the range 1 to 3 or at a high pH in the range 10 to 12.

4. A process for the formation of a photographic emulsion in which an aqueous solution comprising a water-soluble halide, a water-soluble silver salt and a protective colloid is produced in a reactor and silver halide grains are formed in the reactor by reaction of the halide and the silver salt, nucleus formation and crystal growth both taking place in the reactor characterised in that a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000 daltons.

5. A process according to claim 4 characterised in that the mammalian gelatin has a molecular weight in the range 10000 to 20000 daltons.

6. A process according to claim 4 or claim 5 characterised in that the mammalian gelatin has been obtained by treating normal gelatin with a gelatin decomposing enzyme.

7. A process according to claim 6 characterised in that the gelatin decomposing enzyme is trypsin.

8. A process according to claim 4 or claim 5 characterised in that the mammalian gelatin has been obtained by heating normal gelatin either at a low pH in the range 1 to 3 or at a high pH in the range 10 to 12.

9. A process according to any one of claims 4 to 8 characterised in that it is carried out at a temperature in the range 5 to 35 C.

10. A process according to any one of claims 4 to 9 characterised in that the process temperature is controlled to within the range 0.25 to 0.3 degrees C.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 93 20 3293

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X,Y	DATABASE WPI Section Ch, Week 9223, Derwent Publications Ltd., London, GB; Class A12, AN 92187528 & JP-A-4 110 935 (KONICA CORPORATION) 13 April 1992 * abstract *	1-10	G03C1/047 G03C1/015
X,Y	DATABASE WPI Week 9223, Derwent Publications Ltd., London, GB; AN 92187527 & JP-A-4 110 934 (KONICA CORPORATION) * abstract *	1-10	
X,Y	DATABASE WPI Week 9007, Derwent Publications Ltd., London, GB; AN 90048068 & JP-A-2 000 838 (FUJI PHOTO FILM K.K.) * abstract *	1-10	
X,Y	DATABASE WPI Week 8940, Derwent Publications Ltd., London, GB; AN 89289978 & JP-A-1 213 637 (FUJI PHOTO FILM K.K.) * abstract *	1-10	
Y	US-A-5 145 768 (Y. ICHIKAWA ET AL) * column 12, line 25 - column 12, line 48 *	1-10	
A	GB-A-1 177 185 (EASTMAN KODAK COMPANY) * the whole document *	1-10	
A	GB-A-1 173 196 (VEB FILMFABRIK WOLFEN) * the whole document *	1-10	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31 March 1994	Examiner Buscha, A
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			