

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 600 543 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

03.03.1999 Bulletin 1999/09

(51) Int Cl.⁶: **G03C 1/047**, G03C 1/015

(21) Application number: **93203293.1**

(22) Date of filing: **25.11.1993**

(54) **Process for producing silver halide grains**

Verfahren zur Herstellung von Silberhalogenidkörnern

Procédé de production de grains d'halogénure d'argent

(84) Designated Contracting States:
DE FR GB

(30) Priority: **28.11.1992 GB 9224967**

(43) Date of publication of application:
08.06.1994 Bulletin 1994/23

(73) Proprietors:

- **KODAK LIMITED**
Harrow, Middlesex HA1 4TY (GB)
Designated Contracting States:
GB
- **EASTMAN KODAK COMPANY**
Rochester, New York 14650-2201 (US)
Designated Contracting States:
DE FR

(72) Inventors:

- **Bee, John Arthur, Kodak Limited**
Harrow, Middlesex, HA1 4TY (GB)
- **Hartman, Andrew, Kodak Limited**
Harrow, Middlesex, HA1 4TY (GB)

(74) Representative: **Aufflick, James Neil**
Kodak Limited
Patent Department
Headstone Drive
Harrow Middlesex HA1 4TY (GB)

(56) References cited:

GB-A- 1 173 196 **GB-A- 1 177 185**
US-A- 5 145 768

- **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
- **DATABASE WPI Week 9223, Derwent**
Publications Ltd., London, GB; AN 92187527 &
JP-A-4 110 934 (KONICA CORPORATION)
- **DATABASE WPI Week 9007, Derwent**
Publications Ltd., London, GB; AN 90048068 &
JP-A-2 000 838 (FUJI PHOTO FILM K.K.)
- **DATABASE WPI Week 8940, Derwent**
Publications Ltd., London, GB; AN 89289978 &
JP-A-1 213 637 (FUJI PHOTO FILM K.K.)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 600 543 B1

Description

[0001] This invention relates to a process for producing silver halide grains and to a process for the formation of a photographic emulsion.

[0002] 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.

[0003] 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.

[0004] 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.

[0005] 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.

[0006] Japanese patent applications JP-A-2000838 and JP-A-1213637 disclose silver halide emulsions comprising silver halide grains, specifically tabular grains, produced by a process wherein nucleus formation and crystal growth take place in the presence of a low molecular weight gelatin, to provide grains of uniform particle size and monodispersibility.

[0007] Japanese patent applications JP-A-4110934 and JP-A-4110935 disclose the use of a low molecular weight gelatin in a process of nucleus formation and crystal growth of silver halide grains at a temperature of at least 40°C to overcome fog formation and low sensitivity.

[0008] According to the present invention we provide

a process for the production of silver chloride grains in which an aqueous solution comprising a water-soluble chloride, a water-soluble silver salt and a protective colloid is produced in a reactor and silver chloride grains are formed in the reactor by reaction of the chloride and the silver salt, wherein a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000, characterised in that nucleus formation and crystal growth both take place in the reactor and that the process is carried out at a temperature in the range 5 to 35°C.

[0009] Further according to the present invention we provide a process for the formation of a photographic emulsion in which an aqueous solution comprising a water-soluble chloride, a water-soluble silver salt and a protective colloid is produced in a reactor and silver chloride grains are formed in the reactor by reaction of the chloride and the silver salt, wherein a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000, characterised in that nucleus formation and crystal growth both take place in the reactor and that the process is carried out at a temperature in the range 5 to 35°C. The silver chloride grains are produced by reacting an aqueous silver salt solution and an aqueous chloride 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 chloride 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 chloride solution and the aqueous salt solution are added to the solution in the reactor.

[0010] 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 hydrolysed 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.

[0011] 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. According to the

invention the halide used is sodium chloride and the silver salt silver nitrate is preferred. 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 0.2µm (microm).

[0012] 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 chloride 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.

[0013] The invention is illustrated by the accompanying Examples:

EXAMPLE 1

[0014] 2000 ml of an 8% solution of acid hydrolysed gelatin (molecular weight 20000) 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 ml/min to a final rate of 180 ml/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 0.12µm (microm).

EXAMPLE 2

[0015] 2000 ml of an 8% solution of acid hydrolysed gelatin (molecular weight 20000) 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 ml/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 0.055µm (microm) was obtained.

Claims

1. A process for the production of silver chloride grains in which an aqueous solution comprising a water-soluble chloride, a water-soluble silver salt and a protective colloid is produced in a reactor and silver chloride grains are formed in the reactor by reaction of the chloride and the silver salt, wherein a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000, characterised in that nucleus formation and crystal growth both take place in the reactor and that the process is carried out at a temperature in the range 5 to 35°C.
2. A process according to claim 1 characterised in that the mammalian gelatin has a mean molecular weight in the range 10000 to 20000.
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.
4. A process according to claim 1 or claim 2 characterised in that the mammalian gelatin has been obtained by treating normal gelatin at a low pH in the range 1 to 3.
5. A process according to claim 1 or claim 2 characterised in that the mammalian gelatin has been obtained by treating normal gelatin at a high pH in the range 10 to 12.
6. A process for the formation of a photographic emulsion in which an aqueous solution comprising a water-soluble chloride, a water-soluble silver salt and a protective colloid is produced in a reactor and silver chloride grains are formed in the reactor by reaction of the chloride and the silver salt, wherein a major proportion of the protective colloid is a modified mammalian gelatin having a mean molecular weight in the range 5000 to 30000, characterised in that nucleus formation and crystal growth both take place in the reactor and the process is carried out at a temperature in the range 5 to 35°C.
7. A process according to claim 6 characterised in that the mammalian gelatin has a molecular weight in the range 10000 to 20000.
8. A process according to claim 6 or claim 7 characterised in that the mammalian gelatin has been obtained by treating normal gelatin with a gelatin decomposing enzyme.
9. A process according to claim 8 characterised in that the gelatin decomposing enzyme is trypsin.

10. A process according to claim 6 or claim 7 characterised in that the mammalian gelatin has been obtained by heating normal gelatin at a low pH in the range 1 to 3.
11. A process according to claim 6 or claim 7 characterised in that the mammalian gelatin has been obtained by heating normal gelatin at a high pH in the range 10 to 12.
12. A process according to any one of claims 6 to 11 characterised in that the process temperature is controlled to within the range 0.25 to 0.3 degrees C.

Patentansprüche

1. Verfahren zur Herstellung von Silberchloridkörnern, bei dem eine wässrige Lösung mit Wasser-löslichem Chlorid, einem Wasser-löslichen Silbersalz und einem Schutzkolloid in einem Reaktor erzeugt und Silberchloridkörnchen in dem Reaktor erzeugt werden durch Umsetzung des Chlorides und des Silbersalzes, wobei ein Hauptanteil des Schutzkolloides eine modifizierte Säugetier-Gelatine mit einem mittleren Molekulargewicht im Bereich von 5000 bis 30000 ist, dadurch gekennzeichnet, daß die Keimbildung und das Kristallwachstum beide in dem Reaktor stattfinden und daß das Verfahren bei einer Temperatur im Bereich von 5 bis 35°C durchgeführt wird.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Säugetier-Gelatine ein mittleres Molekulargewicht im Bereich von 10000 bis 20000 hat.
3. Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß die Säugetier-Gelatine erhalten wurde durch Behandlung von normaler Gelatine mit dem Gelatine zersetzenden Enzym Trypsin.
4. Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß die Säugetier-Gelatine erhalten wurde durch Behandlung von normaler Gelatine bei einem niedrigen pH-Wert im Bereich von 1 bis 3.
5. Verfahren nach Anspruch 1 oder Anspruch 2, dadurch gekennzeichnet, daß die Säugetier-Gelatine erhalten wurde durch Behandlung von normaler Gelatine bei einem hohen pH-Wert im Bereich von 10 bis 12.
6. Verfahren zur Herstellung einer photographischen Emulsion, bei dem eine wässrige Lösung mit einem Wasser-löslichen Chlorid, einem Wasser-löslichen Silbersalz und einem Schutzkolloid in einem Reak-

tor erzeugt und Silberchloridkörnchen in dem Reaktor erzeugt werden durch Umsetzung des Chlorides und des Silbersalzes, wobei ein Hauptanteil des Schutzkolloides eine modifizierte Säugetier-Gelatine mit einem mittleren Molekulargewicht im Bereich von 5000 bis 30000 ist, dadurch gekennzeichnet, daß die Keimbildung und das Kristallwachstum beide in dem Reaktor erfolgen und das Verfahren bei einer Temperatur im Bereich von 5 bis 35°C durchgeführt wird.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die Säugetier-Gelatine ein Molekulargewicht im Bereich von 10000 bis 20000 hat.
8. Verfahren nach Anspruch 6 oder Anspruch 7, dadurch gekennzeichnet, daß die Säugetier-Gelatine erhalten wurde durch Behandlung von normaler Gelatine mit einem Gelatine zersetzenden Enzym.
9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß das Gelatine zersetzende Enzym Trypsin ist.
10. Verfahren nach Anspruch 6 oder Anspruch 7, dadurch gekennzeichnet, daß die Säugetier-Gelatine erhalten wurde durch Erhitzung von normaler Gelatine bei einem niedrigen pH-Wert im Bereich von 1 bis 3.
11. Verfahren nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß die Säugetier-Gelatine erhalten wurde durch Erhitzung von normaler Gelatine bei einem hohen pH-Wert im Bereich von 10 bis 12.
12. Verfahren nach einem der Ansprüche 6 bis 11, dadurch gekennzeichnet, daß die Prozeß-Temperatur derart gesteuert wird, daß sie innerhalb des Bereiches von 0,25 bis 0,3°C liegt.

Revendications

1. Procédé de production de grains de chlorure d'argent dans lequel on forme une solution aqueuse comprenant du chlorure soluble dans l'eau, un sel argentique soluble dans l'eau et un colloïde protecteur dans un réacteur et on forme des grains de chlorure d'argent dans le réacteur en faisant réagir le chlorure et le sel argentique, dans lequel une proportion majeure de colloïde protecteur est de la gélatine de mammifère modifiée ayant un poids moléculaire moyen compris entre 5 000 et 30 000, caractérisé en ce que la formation des nucléi et la croissance cristalline ont toutes deux lieu dans le réacteur et en ce que le procédé est mis en oeuvre à une température comprise entre 5 et 35°C.

2. Procédé selon la revendication 1, caractérisé en ce que la gélatine de mammifère a un poids moléculaire moyen compris entre 10 000 et 20 000. 6 à 11, caractérisé en ce que la température du procédé est contrôlée dans un intervalle compris entre 0,25 et 0,3°C.
3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'on obtient la gélatine de mammifère en traitant la gélatine normale avec une enzyme trypsine décomposant la gélatine. 5
4. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'on obtient la gélatine de mammifère en traitant la gélatine normale à un faible pH compris entre 1 et 3. 10
5. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'on obtient la gélatine de mammifère en traitant la gélatine normale à un pH élevé compris entre 10 et 12. 15
6. Procédé de formation d'une émulsion photographique dans lequel on forme une solution aqueuse comprenant du chlorure soluble dans l'eau, un sel argentique soluble dans l'eau et un colloïde protecteur dans un réacteur et on forme des grains de chlorure d'argent dans le réacteur en faisant réagir le chlorure et le sel argentique, dans lequel une proportion majeure de colloïde protecteur est de la gélatine de mammifère modifiée ayant un poids moléculaire moyen compris entre 5 000 et 30 000, caractérisé en ce que la formation des nucléi et la croissance cristalline ont toutes deux lieu dans le réacteur et en ce que le procédé est mis en oeuvre à une température comprise entre 5 et 35°C. 20 25 30
7. Procédé selon la revendication 6, caractérisé en ce que la gélatine de mammifère a un poids moléculaire compris entre 10 000 et 20 000. 35
8. Procédé selon la revendication 6 ou 7, caractérisé en ce que l'on obtient la gélatine de mammifère en traitant la gélatine normale avec une enzyme décomposant la gélatine. 40
9. Procédé selon la revendication 8, caractérisé en ce que l'enzyme décomposant la gélatine est la trypsine. 45
10. Procédé selon la revendication 6 ou 7, caractérisé en ce que l'on obtient la gélatine de mammifère en chauffant la gélatine normale à un faible pH compris entre 1 et 3. 50
11. Procédé selon la revendication 6 ou 7, caractérisé en ce que l'on obtient la gélatine de mammifère en chauffant la gélatine normale à un pH élevé compris entre 10 et 12. 55
12. Procédé selon l'une quelconque des revendications