(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 577 886 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **92202114.2**

(22) Date of filing: **10.07.92**

(51) Int. Cl.5: **G03C 1/005**, G03C 1/015

(43) Date of publication of application:
12.01.94 Bulletin 94/02

(84) Designated Contracting States:
BE DE FR GB NL

(71) Applicant: **AGFA-GEVAERT naamloze vennootschap**
Septestraat 27
B-2640 Mortsel(BE)

(72) Inventor: **Verbeeck, Ann c/o Agfa-Gevaert N.V.**
DIE 3800
Septestraat 27
B-2640 Mortsel(BE)

(54) Preparation of tabular grain emulsions with intermediate aspect ratio.

(57) A method is disclosed for the preparation of emulsions containing tabular grains with moderate aspect ratio and good monodispersity comprising following steps :

- performing a nucleation step, a physical ripening step, at least one growth step at a pBr value lower than 2,
- concentrating the reaction mixture volume by ultrafiltration during the precipitation steps in such a way that, at any moment when said ultrafiltration is applied, the ultrafiltration flux is equal to or greater than the sum of the flow rates of the silver ion and halogenide ion solutions.

EP 0 577 886 A1

1. Field of the invention.

The present invention relates to a method for the preparation in a cost-effective way of a photographic silver (iodo)bromide emulsion with tabular grains showing an intermediate aspect ratio and a low coefficient of variation of their grain size distribution.

2. Background of the invention.

Tabular grains are known in the photographic art for quite some time. As early as 1961 Berry et al described the preparation and growth of tabular silver bromoiodide grains in Photographic Science and Engineering, Vol 5, No 6. A discussion of tabular grains appeared in Duffin, Photographic Emulsion Chemistry, Focal Press, 1966, p. 66-72. Early patent literature includes Bogg US Patent 4,063,951, Lewis US Patent 4,067,739 and Maternaghan US Patents 4,150,994; 4,184,877 and 4,184,878. However the tabular grains described herein cannot be regarded as showing a high diameter to thickness ratio, commonly termed aspect ratio. In a number of US Patent Applications filed in 1981 and issued in 1984 tabular grains with high aspect ratio and their advantages in photographic applications are described. So Wilgus US Patent 4,434,226 discloses tabular silver bromoiodide grains having a thickness less than 0.2 μm, a diameter of at least 0.6 μm and an average aspect ratio greater than 8:1 and accounting for at least 50 percent of the total projected area of all the emulsion grains. Kofron US Patent 4,439,520 discloses similar grains which are spectrally sensitized. Abbott US Patent 4,425,425 describes radiographic materials containing tabular grains with an aspect ratio of at least 8:1 and Abbott US Patent 4,425,426 discloses similar grains with an aspect ratio between 5:1 and 8:1. A survey on high aspect ratio silver halide emulsions appeared in Research Disclosure, Volume 225, Jan 1983, Item 22534.

The benefits of high aspect ratio tabular grains can be summarized as follows. Thanks to their particular morphology, greater amounts of spectral sensitizers can be adsorbed per mole silver halide compared to classical globular grains. As a consequence such spectrally sensitized tabular grains show an improved speed-granularity relationship and a wide separation between their blue speed and minus blue speed. Sharpness of photographic images can be improved using tabular grains thanks to their lower light scattering properties again compared to conventional globular emulsion grains. In color negative materials the conventional sequence of the light sensitive layers can be altered and the yellow filter layer can be omitted. In developed black-and-white images high covering power is obtained even at high hardening levels; alternatively reduced silver halide coverages can be achieved if wanted resulting again in improved sharpness. In double coated radiographic materials the presence of tabular grains reduces the so-called cross-over which is the dominant factor for sharpness in such materials.

However high aspect ratio tabular grains show some disadventages and a more moderate aspect ratio can be desirable for particular applications. High aspect ratio tabular grain emulsions tend to produce a reddish-brown colour hue on development. This is very disturbing when the emulsion is incorporated in a radiographic material in which case the radiologist interpreting the developed image is accustomed to the more neutral hue of developed conventional globular grains. So for this application tabular grain emulsions showing an intermediate aspect ratio, e.g. between 2 and 8 are more suitable because they give a more neutral grey on development while at least partly preserving the specific adventages of tabular grains. This intermediate aspect ratio is preferably combined with a low coefficient of variation on the grain size frequency distribution, in other words a good monodispersity, resulting in high gradation and excellent sharpness.

Monodisperse emulsions on the other hand show the advantages of high gradation, good sharpness and excellent reproducibility. Because of the photographic benefits of on one hand monodisperse emulsions and on the other hand tabular grain emulsions, it was obvious that emulsion technologist tried and still try to combine the advantages of both classes.

Several patent publications reveal methods for preparing monodispers tabular grain emulsions. So Mignot US 4,386,156 describes a method for the preparation of tabular grains with a variance of less than 30 % by transforming cubic seed crystals into tabular grains. Saitou DE 3 707 135 discloses hexagonal tabular grains with a low coefficient of variation by taking certain defined measures in the precipition and physical ripening stages. Nottorf US 4,722,866 discloses a preparation method for tabular grains with narrow size distribution by a rather complex precipitation process comprising at least five distinct stages. Zola EP 0 362 699 describes silver bromoiodide grains with an average aspect ratio greater than 12 characterized in that the quotient of the average aspect ratio of the tabular grains divided by the coefficient of variation of the total grain population is greater than 0.7. In this way the monodispersity is correlated with the aspect ratio because of the greater difficulty of preparing monodisperse tabular grains with very high aspect ratios.

An essential feature of the preparation method consists in a nucleation stage characterized by a very high flow rate and concentrated solutions. Still other methods are disclosed in US 4,977,0774 and EP 0 391 560. In European Patent Application, filed on 20 Febr. 1992 under Application No. 92200498, a method is described for preparing an emulsion containing a monodispers tabular grain fraction by using an aminoazaindene as crystal growth modifier. However this method can give rise to development problems.

Most of the patents cited above do not combine however monodispersity with the feature of intermediate aspect ratio. Methods to prepare tabular grains with increased thickness, resulting in the desired moderate aspect ratio, have already been disclosed in EP 0 391 560 cited above and in US 4,801,522, but both methods make use of an ammoniacal base solution making the process difficult to control and unecological. US 5,013,641 claims a method for the preparation of relative thick tabular grains, the method including a pH increase to a value greater than 9 before emulsion digestion. In the teaching of European Patent Application, filed 5 May 1992 under Eurpean Application Number 92201259, the aspect ratio is controlled by performing a pBr jump between the first and second crystal growth step. However the two latter methods tend to increase the fog of the finished emulsion.

Another important aspect of emulsion preparation in general, not restricted to tabular grains, is an economic one. In order to manufacture emulsions in a cost-effective way the so-called kettle yield should be maximized, meaning a minimal end volume of the precipitation mixture for a maximal amount of precipitated silver halide. Mignot US 4,334,012 discloses an elegant way of concentrating the reaction mixture volume in the kettle by applying the well-known emulsion washing technique known as ultrafiltration in a continuous way during the precipitation steps. The teachings of Mignot do not include specific examples on tabular grain or monodispers emulsion preparation.

It is an object of the present invention to provide a method for the preparation of silver (iodo)bromide tabular grain emulsions with a moderate aspect ratio.

It is a further object of the present invention to provide a method for preparing such tabular grain emulsions showing a low coefficient of variation on the grain size distribution.

It is a still further object of the present invention to provide a method of preparing said tabular grain emulsions in a cost-effective way.

3. Summary of the invention.

The objects of the present invention are realized by providing a method for the preparation of a photographic silver (iodo)bromide emulsion containing tabular grains wherein at least 70 % of the total projected area of all grains is occupied by said tabular grains, and wherein said tabular grain fraction exhibit :

- an average aspect ratio comprised between 2 and 8,
- a coefficient of variation on the tabular grain size distribution lower than 0.30,

said method comprising following steps :

- performing a nucleation step during which at most 5 % of the total silver halide is precipitated,
- performing a physical ripening step,
- performing at least one growth step characterized by a pBr value lower than 2,
- concentrating the reaction mixture volume by ultrafiltration during the precipitation steps in such a way that at any moment when ultrafiltration is applied the ultrafiltration flux is equal to or greater than the sum of the flow rates of the silver ion and halogenide ion solutions.

It was found unexpectedly that the application of such ultrafiltration procedure during precipitation, beside its favourable economic aspect, promoted the monodispersity and the intermediate aspect ratio character of the obtained tabular grain emulsion. More explicitly, it was found that systematically reducing the end volume per unit amount of silver halide precipitated promoted a systematic decrease in average aspect ratio and a decrease in coefficient of variation.

4. Detailed description of the invention.

The precipitation includes a nucleation step and at least one growth step alternated by at least one physical ripening step.

The dispersion medium is characterized by a gelatin concentration between 0.01 and 1 percent, a temperature preferably not exceeding 45 °C and a pAg corresponding to an electrochemical potential preferably varying between -3 and -90 mV measured with a silver electrode versus a standard calomel electrode. Additional gelatin can be added at a later stage of the emulsion preparation, e.g. before growth, after precipitation before chemical sensitization, or before coating in order to establish optimal coating

conditions and/or to establish the required thickness of the coated emulsion layer. The relative volume of the dispersion medium may not be excessive in order to allow an end amount of at least 2 moles silver halide precipitated per liter end volume of the reaction mixture.

Of the total silver halide preferably 0.5 % to 5.0 % is precipitated during the nucleation step while the rest of the silver and halide salts is added during one or more consecutive double jet growth steps.

The nucleation stage is characterized by very high flow rates leading to high local supersaturation, a temperature maintained at a value preferably not exceeding 45 °C, and a pAg between -3 and -90 mV, preferably between -33 and -75 mV. The physical ripening step between the nucleation stage and the first growth step is characterized by an increase in the gelatin concentration to at most 3 % ; the temperature is risen to preferably at least 70 °C and the pAg is maintained in the same range as in the nucleation stage. In this way parallel twins are selectively grown out. During the growth step(s) an increasing flow rate of silver and halide solutions is preferably established, e.g. a linearly increasing flow rate. Typically the flow rate at the end is about 3 to 5 times greater then at the start of the growth step. Alternatively the flow rate can vary according to a quadratic equation as disclosed in DE 2107118, or to another exponential equation. As still a further alternative several consecutive growth steps are established with consecutively increasing increments of the linaerly increasing fow rates. In this way a quadratic or exponential increment of the flow rate can be simulated. These flow rates can be monitored by e.g. magnetic valves. During the growth step-(s) the pAg is maintained at a constant value corresponding to a silver potential between -3 and -60 mV. The pH is preferably established at a value between 4.0 and 9.0. Due to the concentrating effect of the continuous ultrafiltration the gelatin concentration is kept preferably between 1 % and 2 %. Under the described precipitation conditions no additional twin crystals are formed anymore but the anisotropic growth of existing crystals with parallel twin planes is promoted.

An essential feature of the present invention is the application of ultrafiltration during the precipitation steps in such a way that, when applied, the permeate flux of the aqeous salt solution which is pouring through the ultrafiltration membrane, is at any moment equal to or greater than the sum of the flow rates of the silver ion and halide ion solutions. This ultrafiltration or membrane flux is a function of the total operative surface of the membrane and the trans-membrane pressure. In a preferred embodiment the ultrafiltration flux is constant and equal or slightly greater than the sum of the maximal flow rates of the silver and halide ion solutions. Preferably the ultrafiltration procedure is applied in a continuous way during the precipitation steps, but, if necessary, it can be interrupted for short periods. During physical ripening preferably no ultrafiltration is applied. By applying the ultrafiltration procedure the total reaction mixture volume can be lowered during the precipitation. Alternatively the reaction mixture volume can be readjusted, e.g. kept constant by the application of an additional jet of water. By the methods described it is possible to limit the end precipitation volume, for 3 moles of silver halide precipitated, to about 1 liter or even to 0.5 l instead of to about 5 - 6 liter of a conventional precipitation scheme when no ultrafiltration is applied. This achievement could not have been reached by solely concentrating the silver ion and halide ion jets. In a preferred embodiment the ultrafiltration module is conceived in such a way that the total volume of the ultrafiltration module and of its connecting means, is lower than 1/3 of the total precipitation volume. Moreover the circulation flux through the ultrafiltration module preferably is high enough, as to achieve a delay time in the module of any liquid volume unit of lower than 60 seconds and, most preferably lower than 30 seconds. Even delay times as low as 10 seconds can be achieved. It was stated experimentally that this factor was important in order to achieve good monodispersity of the tabular grains.

A preferred ultrafiltration module for the practice of this invention is a ROMICON HF2-20-PM10, provided with a MASTERFLEX pump. For a typical precipitation (see examples) wherein the flow rate of the silver ion jet during the growth step(s) is linearly increased to an end rate of 25 ml/min a constant flux of about 50 ml/min is applied. But in the case of more strongly increasing flow rates, e.g. qudratically increasing flow rates, a flux of about 200 ml/min can be established if needed. As stated above the kettle volume can be readjusted, e.g. kept constant, by the application of an extra jet of water.

The emulsions containing tabular grains prepared according to the method of the present invention can be used in various types of photographic elements. However because of their (iodo)bromide composition they are preferably used in those applications for which high sensitivity is required. Preferred embodiments include black-and-white or colour negative recording materials for still photography or for cinematographic application, black-and-white or colour reversal materials, graphic arts camera sensitive films. However their incorporation in radiographic recording materials constitutes the most preferred embodiment, thanks to the neutral hue of the developed tabular grains as was explained above.

The iodide content of the tabular grains prepared according to the invention is limited to about 15 %, and for the preferred application in a radiographic material, is preferably comprised between 1 % and 5 %.

The photographic element containing one or more emulsions prepared in accordance with the present invention can be composed of one single emulsion layer, as is the case for many applications, or it can be built up by two or even more emulsion layers. In the preferred embodiment of a radiographic recording material two identical emulsion layers can be applied on both sides of the support. In the case of colour photography the material contains blue, green and red sensitive layers each of which can be single or multiple. Beside the light sensitive emulsion layer(s) the photographic material can contain several non-light sensitive layers, e.g. a protective layer, one or more backing layers, one or more subbing layers, and one or more intermediate layers e.g. filter layers.

The emulsions containing tabular silver (iodo)bromide grains prepared in accordance with the present invention can be chemically sensitized as described e.g. in "Chimie et Physique Photographique" by P. Glafkides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature chemical sensitization can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines. The emulsions can be sensitized also by means of gold-sulphur ripeners or by means of reductors e.g. tin compounds as described in GB 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds.

The tabular silver (iodo)bromide emulsions under consideration can be spectrally sensitized with methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes and complex merocyanine dyes. A survey of useful chemical classes of spectral sensitizing dyes and specific useful examples in connection with tabular grains is given in Research Disclosure Item 22534. In classical emulsion preparation spectral sensitization traditionally follows the completion of chemical sensitization. However, in connection with tabular grains, it is specifically considered that spectral sensitization can occur simultaneously with or even precede completely the chemical sensitization step. For example, Maskasky US Ser. No 431,855, titled CONTROLLED SITE EPITAXIAL SENSITIZATION discloses the chemical sensitization after spectral sensitization at one or more ordered discrete edge sites of tabular grains. This can be done with the tabular grains containing emulsions of the present invention.

The emulsion layer(s) in accordance with the present invention or the non-light-sensitive layers may comprise compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of the photographic elements or during the photographic treatment thereof. Many known compounds can be added as fog-inhibiting agent or stabilizer to the silver halide emulsion. Suitable examples are e.g. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JA-Appl. 75-39537, and GB 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US 4,727,017, and other compounds such as benzenethiosulphonic acid, toluenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide. Other compounds that can be used as fog-inhibiting compounds are metal salts such as e.g. mercury or cadmium salts and the compounds described in Research Disclosure N° 17643 (1978), Chapter VI.

In the specific embodiment of a colour negative or colour reversal photographic material, the usual ingredients specific for colour materials can be present e.g. colour couplers, couplers bearing a releasable photographic useful group and scavengers for oxidized developer. These typical ingredients for colour materials can be soluble or added in dispersed form, e.g. with the aid of so-called oilformers or they can be added in polymeric latex form.

The gelatin binder of the photographic elements can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1,3-vinylsulphonyl-2-propanol, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methylol-dimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-

triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binder can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US 4,063,952 and with the onium compounds as disclosed in EP 0 408 143.

The photographic element used in connection with the present invention may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulpho, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification and as compounds preventing or reducing adhesion. Preferred surface-active coating agents are compounds containing perfluorinated alkyl groups.

The photographic element in connection with the present invention may further comprise various other additives such as e.g. compounds improving the dimensional stability of the photographic element, UV-absorbers, spacing agents and plasticizers.

As stated above the photographic material can contain several non light sensitive layers, e.g. an anti-stress top layer, one or more backing layers, and one or more intermediate layers eventually containing filter-or antihalation dyes that absorb scattering light and thus promote the image sharpness. Suitable light-absorbing dyes are described in e.g. US 4,092,168, US 4,311,787, DE 2,453,217, and GB 7 907 440. One or more backing layers can be provided at the non-light sensitive side of the support. These layers which can serve as anti-curl layer can contain e.g. matting agents like silica particles, lubricants, antistatic agents, light absorbing dyes, opacifying agents, e.g. titanium oxide and the usual ingredients like hardeners and wetting agents.

The support of the photographic material may be opaque or transparent, e.g. a paper support or resin support. When a paper support is used preference is given to one coated at one or both sides with an Alpha-olefin polymer, e.g. a polyethylene layer which optionally contains an anti-halation dye or pigment. It is also possible to use an organic resin support e.g. cellulose nitrate film, cellulose acetate film, poly-vinylacetal) film, polystyrene film, polyethylene terephthalate film, polycarbonate film, polyvinylchloride film or poly-Alpha-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.07 and 0.35 mm. These organic resin supports are preferably coated with a subbing layer which can contain water insoluble particles such as silica or titanium dioxide.

The photographic material containing tabular grains prepared according to the present invention can be image-wise exposed by any convenient radiation source in accordance with its specific application. Of course processing conditions and composition of processing solutions are dependent from the specific type of photographic material in which the tabular grains containing emulsions prepared according to the present invention are applied. Preferably an automatically operating processing apparatus is used provided with a system for automatic regeneration of the processing solutions.

The following examples illustrate the invention without however limiting it thereto.

EXAMPLES

EXAMPLE 1

A. Preparation of tabular grain emulsions according to the invention.

All precipitation schemes were expressed on a base of 1000 ml 2.94 molar $AgNO_3$ (solution A) corresponding to a total amount of 500 g $AgNO_3$ added.

Control emulsion 1

The following solutions were prepared :

- a dispersion medium (C) consisting of 3120 ml demineralized water, 12.6 g of inert gelatin and 53 ml of a 2.94 molar potassium bromide solution; the temperature was established at 45 °C and pH was adjusted to 4.5; the pAg corresponded to an electrochemical potential of -63 mV measured with a silver electrode versus standard calomel;
- 1000 ml of a 2.94 molar silver nitrate solution (A);
- a mixture of a solution of 2.94 molar potassium bromide and 2.94 molar potassium iodide at a ratio of 99/1 (B).

A nucleation step was performed by introducing solution A and solution B simultaneously in dispersion medium C both at a flow rate of 25 ml/min during 28 seconds. After a physical ripening time of 15 minutes during which the temperature was risen to 70 °C, 48 g of phtaloylated gelatin, dissolved in 432 ml of water, was added and the mixture was stirred for an additional 5 minutes. Then a first growth step was performed by introducing simultaneously during 564 seconds solution (A) at a flow rate of 5 ml/min and solution B in such a way that a constant silver potential of -33 mV is maintained. Then a second growth step was performed by introducing by a double jet during 3763 seconds solution A starting at a flow rate of 5 ml/min and linearly increasing the flow rate to an end value of 25 ml/min, and solution B at an increasing flow rate as to maintain a constant silver potential value of -33 mV.

No ultrafiltration technique was used during the precipitation so that the end volume of the reaction mixture was about 6 l.

Control emulsion 2

The precipitation scheme was identical to emulsion 1 with the exception that during the two growth steps the silver potential was maintained at -3 mV instead of -33 mV.

Since no precipitation technique was used the end volume of the reaction mixture was again about 6 l.

Control emulsion 3

The following solutions were prepared :

- a dispersion medium (C) consisting of 2127 ml demineralized water, 12.5 g of inert gelatin and 36 ml of a 2.94 molar potassium bromide solution; the temperature was established at 50 °C and the pH was adjusted to 5.8; the pAg corresponded to an electrochemical potential of -63 mV measured with a silver electrode versus standard calomel;
- 1500 ml of a 1.96 molar silver nitrate solution (A);
- a mixture of a solution of 1.96 molar potassium bromide and 1.96 molar potassium iodide at a ratio of 99/1.

A nucleation step was performed by introducing solution A and solution B simultaneously in dispersion medium C both at a flow rate of 46.8 ml/min during 28 seconds. After a physical ripening time of 20 minutes during which the temperature was risen to 70 °C, 47.5 g of phtaloylated gelatin, dissolved in 475 ml of water, was added and the mixture was stirred for an additional 10 minutes. Then a first growth step was performed by introducing simultaneously during 174 seconds solution (A) at a flow rate of 7.5 ml/min and solution B in such a way that a constant silver potential of -33 mV is maintained. Then a second growth step was performed by introducing by a double jet during 1944 seconds solution A starting at a flow rate of 7.5 ml/min and linearly increasing the flow rate to an end value of 24 ml/min, and solution B at an increasing flow rate as to maintain a constant silver potential value of -33 mV. A second physical ripening stage lasted 348 seconds. Then the pAg was switched to a value corresponding to a silver potential of +60 mV by a single jet of solution A during 462 seconds. Finally a third growth step was performed by introducing by a double jet during 2246 seconds solution A starting at a flow rate of 7.5 ml/min and linearly increasing the flow rate to an end value of 37.5 ml/min, and solution B at an increasing flow rate as to maintain a constant silver potential value of +60 mV.

Since no ultrafiltration technique was used the end volume of the reaction mixture again was about 6 l.

Invention emulsion 4

The following solutions were prepared :

- a dispersion medium (C) consisting of 750 ml demineralized water, 4.04 g of inert gelatin and 12.7 ml of a 2.94 molar potassium bromide solution; the temperature was established at 45 °C and pH was adjusted to 4.5; the pAg corresponded to an electrochemical potential of -63 mV measured with a silver electrode versus standard calomel;
- 1000 ml of a 2.94 molar silver nitrate solution (A);
- a mixture of a solution of 2.94 molar potassium bromide and 2.94 molar potassium iodide at a ratio of 99/1 (B).

A nucleation step was performed by introducing solution A and solution B simultaneously in dispersion medium C both at a flow rate of 25 ml/min during 28 seconds. After a physical ripening time of 15 minutes during which the temperature was risen to 70 °C, 13.02 g of phtaloylated gelatin, dissolved in 250 ml of water, was added and the mixture was stirred for an additional 5 minutes. Then a first growth step was performed by introducing simultaneously during 564 seconds solution (A) at a flow rate of 5 ml/min and solution B in such a way that a constant silver potential of -33 mV is maintained. Then a second growth step was performed by introducing by a double jet during 3763 seconds solution A starting at a flow rate of 5 ml/min and linearly increasing the flow rate to an end value of 25 ml/min, and solution B at an increasing flow rate as to maintain a constant silver potential value of -33 mV.

Ultrafiltration was applied during the precipitation steps. The trans-membrane flux amounted to a constant 50 ml/min. The reaction mixture volume was maintained at a constant level by means of an extra water jet. The circulation rate of the kettle mixture through the ultrafiltration module was 2 liter/min. The dead volume was 250 ml. Thanks to this ultrafiltration procedure the end volume of the reaction mixture was reduced to about 1 l instead of about 6 l.

Invention emulsion 5

The precipitation scheme was identical to emulsion 4 with the exception that during the two growth steps the silver potential was maintained at -3 mV instead of -33 mV. The end volume was likewise about 1 l.

Invention emulsion 6

The following solutions were prepared :

- a dispersion medium (C) consisting of 750 ml demineralized water, 4.04 g of inert gelatin and 12.7 ml of a 2.94 molar potassium bromide solution; the temperature was established at 45 °C and pH was adjusted to 4.5; the pAg corresponded to an electrochemical potential of -63 mV measured with a silver electrode versus standard calomel;
- 1000 ml of a 2.94 molar silver nitrate solution (A);
- a mixture of a solution of 2.94 molar potassium bromide and 2.94 molar potassium iodide at a ratio of 99/1 (B).

A nucleation step was performed by introducing solution A and solution B simultaneously in dispersion medium C both at a flow rate of 25 ml/min during 28 seconds. After a physical ripening time of 15 minutes during which the temperature was risen to 70 °C, 13.02 g of phtaloylated gelatin, dissolved in 250 ml of water, was added and the mixture was stirred for an additional 5 minutes. Then a first growth step was performed by introducing simultaneously during 425 seconds solution A starting at a flow rate of 5 ml/min and linearly increasing the flow rate to an end value of 25 ml/min, and solution B at an increasing flow rate as to maintain a constant silver potential value of -33 mV. A second growth step was performed by introducing simultaneously during 440 seconds solution A starting at a flow rate of 25 ml/min and linearly increasing the flow rate to an end value of 56 ml/min, and solution B at an increasing flow rate as to maintain a constant silver potential value of -33 mV. A third growth step was performed by introducing simultaneously during 445 seconds solution A starting at a flow rate of 56 ml/min and linearly increasing the flow rate to an end value of 100 ml/min, and solution B at an increasing flow rate as to maintain a constant silver potential value of -33 mV.

By applying continuous ultrafiltration during precipitation the end volume of the reaction mixture was reduced to about 1 l.

Invention emulsion 7

The precipitation scheme was identical to emulsion 6 with the exception that during the three growth steps the silver potential was maintained at -3 mV instead of -33 mV. The end volume was likewise about 1 liter.

B. Crystallographic characteristics of the prepared emulsions.

The chacteristics of the control emulsions 1 to 3, and of the invention emulsions 4 to 7 are represented in table 1 :

TABLE 1

emulsion	UF	ds	v_{ds}	dEM	th	AR	v_{dEM}
em. 1	-	0.64	0.42	1.42	0.12	13	0.32
inv. em. 4	+	0.59	0.38	1.36	0.19	6.7	0.26
inv. em. 6	+	0.60	0.31	1.25	0.19	6.5	0.18
contr. em. 2	-	0.57	0.46	1.33	0.13	10	0.15
inv. em. 5	+	0.59	0.38	1.36	0.23	4.8	0.15
inv. em. 7	+	0.33	0.31	0.75	0.23	3.3	0.17
contr. em. 3	-	0.69	0.30	1.32	0.20	6.6	0.30

Notes :

ds : average sphere-equivalent diameter in micron of the entire grain population, the sphere-equivalent diameter being defined as the diameter of a hypothetical spherical grain with the same volume as the actual non-spherical grain;

v_{ds} :coefficient of variation or variance of the sphere-equivalent diameter distribution of the entire grain population, defined as the standard deviation of said sphere-equivalent diameter distribution divided by the average sphere-equivalent diameter;

dEM :average electron microscopic diameter in micron of the tabular grain fraction, the electron microscopic diameter being defined as the diameter of a circle having an area equal to the projected area of the actual tabular grain as viewed on an electron photomicrograph;

th : average thickness of the tabular grain fraction as deduced from electron photomicrography;

AR : average aspect ratio of the tabular grain fraction, defined as the average electron microscopic diameter of the tabular grain fraction divided by the average thickness of the tabular grain fraction as deduced from electron photomicrography;

v_{dEM}:coefficient of variation or variance of the electron microscopic diameter disribution of the tabular grain fraction, defined as the standard deviation of said electron microscopic diameter distribution divided by the average electron microscopic diameter.

As can be seen from table 1 the invention emulsions show a reduced average aspect ratio compared to the corresponding control emulsions, and a good monodispersity.

C. Sensitometric results.

As can be seen from table 1 the crystallographic characteristics of control emulsion 3 and invention emulsion 4 are alike, in which case a sensitometric comparison makes sense. These emulsions were chemically ripened to an optimal fog-sensitivity ratio by means of conventional sulphur + gold ripening agents. Then these emulsions were coated at both sides of the support at a total coverage of 7 g Ag/m^2, expressed as $AgNO_3$. After exposure by tungsten light through a continuous wedge samples of the coatings were processed in a conventional hydroquinone-Phenidone developer, fixed in a conventional fixer and dried. The sensitometric characteristics were measured and are represented in table 2.

TABLE 2

emulsion	sensitometric characteristics			
	fog	(S)[1]	gradation	Dmax
contr. em. 3	0.31	1.55	3.26	4.07
inv. em. 4	0.20	1.52	2.99	3.49

note 1 : sensitivity expressed as relative log Et ; lower figure means higher sensitivity.

As can be seen from table 1 the invention emulsion shows the better fog for a comparable sensitivity.

EXAMPLE 2

Another set of emulsions (A to F) was prepared using similar precipitation conditions (pAg, T, flow rates) as was the case with emulsion 1 of example 1, but, going from A to F, the end volume was systematically reduced. During each precipitation the reaction mixture volue was kept constant by choosing appropriate ultrafiltration conditions. The crystallographic chacteristics of the tabular grain fraction of the obtained emulsions are summarized in table 3.

TABLE 3

emulsion	end amount AgX / 1 l	dEM	v_{dEM}	th	AR
A	1 mole	1.66	0.22	0.15	11.3
B	2 moles	1.39	0.19	0.12	11.8
C	3 moles	1.21	0.23	0.18	6.9
D	4 moles	1.14	0.15	0.25	4.6
E	5 moles	0.96	0.17	0.29	3.3
F	6 moles	1.08	0.17	0.29	3.4

As can be seen from table 3 the average aspect ratio is systematically lowered as the end amount per liter of preciptated silver halide is increased.

Claims

1. Method for the preparation of a photographic silver (iodo)bromide emulsion containing tabular grains wherein at least 70 % of the total projected area of all grains is occupied by said tabular grains, and wherein said tabular grain fraction exhibit :

- an average aspect ratio comprised between 2 and 8,
- a coefficient of variation on the tabular grain size distribution lower than 0.30,

said method comprising following steps :

- performing a nucleation step by at least a double jet of silver ion and halide ion solutions during which at most 5 % of the total silver halide is precipitated,
- performing a physical ripening step,
- performing at least one growth step using at least a double jet of silver ion and halide ion solutions characterized by a pBr value lower than 2,
- concentrating the reaction mixture volume by ultrafiltration during the precipitation steps in such a way that, at any moment when said ultrafiltration is applied, the ultrafiltration flux is equal to or greater than the sum of the flow rates of the silver ion and halogenide ion solutions.

2. Method according to claim 1 wherein, at any moment when said ultrafiltration is applied, said ultrafiltration flux remains constant and is equal to or greater than the sum of the maximal flow rates of the silver ion and halide ion solutions.

3. Method according to claim 1 or 2 wherein in addition to said silver and halide ion solutions a jet of water is applied.

4. Method of claim 3 wherein the flow rate of said water jet is regulated in such a way that the reaction mixture volume is kept constant.

5. Method according to any of claims 1 to 4 wherein the precipitation conditions and the ultrafiltration conditions are regulated in such a way that an end amount of silver halide precipitated between 2 moles and 6 moles is obtained per liter end volume of the reaction mixture.

6. Method according to any of claims 1 to 5 wherein the total volume of the ultrafiltration apparatus, composed of its own volume and connecting means, is lower than 1/3 of the total precipitation volume.

7. Method according to any of claims 1 to 6 wherein the flow rates of said silver and halide solutions are increased in a linear way during the growth step(s).

8. Method according to any of claims 1 to 6 wherein the flow rates of said silver and halide solutions are increased in a quadratic way during the growth step(s).

9. Photographic material comprising a support and at least one emulsion emulsion layer characterized in that said emulsion layer contains tabular silver iodobromide grains prepared according to the method of claims 1 to 8.

10. Photographic material according to claim 9 wherein said photographic material is a radiographic material.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2114

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)
A	EP-A-0 423 538 (MINNESOTA MINING AND MANUFACTURING COMPANY) * page 5, line 27; claims 1-6 *	1-10	G03C1/005 G03C1/015
A	EP-A-0 222 252 (AGFA-GEVAERT AKTIENGESELLSCHAFT) * claims; p.5, l.53 - p.6, l.6 *	1-10	
A	US-A-4 334 012 (A.G.E.MIGNOT) * column 7, line 49 - line 52; claims 1-27 *	1-10	
A	US-A-4 336 328 (B.M.BROWN ET AL.) * claims 1-16 *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 MARCH 1993	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

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

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

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)