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(54) Method of preparing a silver chlorobromide emulsion

(57) The invention relates to a method of preparing regular shaped non-tabular high chloride silver halide host crystals, more particularly host crystals on which silver bromide is selectively deposited on the edges and/or corners of said host crystals. Silver halide crystals are prepared, which exhibit excellent high intensity reciprocity law failure and are suitable for high intensity, short time exposure. The method comprises a nucleation and a growth step in which a first peptizer having a binding capacity to silver ions of less than 55 milliVolts measured at pH 5 and a second peptizer having a binding capacity to silver ions of at least 55 milliVolts measured at pH 5 are present during at least the growth step.

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Description

Field of the invention

[0001] The invention relates to a method of preparing regular shaped non-tabular high chloride silver halide host crystals, more particularly host crystals on which silver bromide is selectively deposited on the edges and/or corners of said host crystals. The invention especially concern silver halide crystals, which exhibit excellent high intensity reciprocity law failure and are suitable for high intensity, short time exposure.

Background of the invention

[0002] Imaging systems utilizing digital printing techniques are more widely available in response to market demands for faster processing of photographic prints. In such systems film negatives are scanned and the obtained pixel data are stored in a file, which is subsequently used to control a high-energy output exposure device such as a cathode ray tube (CRT), a light emitting diode (LED) or a laser. The pixel data can be edited using commercially available software like Adobe Photoshop® to obtain an enhanced or preferred image. A known problem when exposing photographic papers with such digital printing techniques is the high intensity reciprocity law failure (HIRLF). The reciprocity law failure (RLF) states that at high intensity exposure, absorption of photons by the silver halide crystals, does not lead to the formation of image, because the crystal is not able to 'process' a high amount of photons in a short time. In conventional systems building shallow electron-traps like iridium into the silver halide crystals reduces this problem, but this does not solve the problem sufficiently for digital exposure techniques. The theory on reciprocity law failure is explained in detail in Tani: Photographic Sensitivity, Oxford University Press 1995, chapter 4.

[0003] Since in the market also conventional techniques are still widely used, the preference is towards photographic print papers that can be utilized by both systems in order to avoid logistic difficulties like high storage volumes.

[0004] Fast development after exposure requires the use of high chloride silver halide crystals, with an overall chloride concentration of at least 50mole percent based on total silver, since these have a higher solubility product than silver bromide or iodide crystals. Such high chloride crystals have insufficient sensitivity. EP 0273404 B1 describes a silver-bromochloride emulsion in which host crystals with high silver chloride content have local phases that have a high silver bromide content deposited onto said host crystals and are chemically sensitised with gold and sulphur. The mechanism of preparing said silverbromochloride emulsions is explained in Sugimoto and Miyake, J. of Colloid and Interface Science, 1990, vol 140, 335-347.

[0005] Such silverbromochloride crystals have the high developing speed of the silver chlorides while retaining the high sensitivity of silver bromide. US 5,200,310 is an improvement of such a high chloride silverbromochloride crystals, utilizing iridium complexes during precipitation of the high bromide local phase on the edges or comers of the high chloride host crystals. Although the addition of iridium improves the reciprocity law failure, it is not sufficiently improved for digital printing techniques using high intensity exposure.

[0006] The use of gold sensitisation can further improve high intensity reciprocity law failure as disclosed in EP 0750220 A2, application US 2001-003037 and Tani, Photographic sensitivity, Oxford University press, 1995, chapter 6. It is well known that the improvement of high intensity reciprocity law failure by gold sensitization comes form the reduced minimum size of developable latent image. However, it is also known that such a smaller latent image is more sensitive to process variations such as temperature and humidity during printing. A known disadvantage of using gold sensitization is that of increased fog, making it necessary to add reducing compounds during the preparation of gold sensitised emulsions. As a result preparation time of a gold sensitised emulsion is much longer than sulphur sensitised emulsions.

[0007] Another problem occurring in photographic emulsions is the latent image stability. It is known that after exposure the latent image in contemporary emulsions remains stable for several hours to days. Developing prints within this period of time will yield therefore a stable result. However, with modern automatic printing equipment using high intensity exposure the latent image stability, prints are developed within minutes after exposure. Prior art does not disclose the problem of such a short time latent image stability within this time span. More specific, the problem which is observed in short periods after exposure is that of the so-called latensification. Contrary to longer term latent image stability, in which latent image fades in time, latensification is the phenomenon by which the latent image is still growing even after exposure was stopped.

[0008] In spite of the prior art attempts to improve the properties of silver halide emulsions at high intensity exposure there still remains a need for silver halide emulsions with high processability which are suitable for both conventional and digital exposure.

Summary of the invention

[0009] The object of the present invention is to provide a silver halide photographic material suitable for rapid processing with excellent high intensity reciprocity law failure while keeping good short time latent image stability.

[0010] It is also an objective of this invention to provide a silver halide photographic material with high sensitivity and low fog.

[0011] It is a further object of this invention to achieve these improvements without further increasing the process time of the improved silver halide emulsion.

[0012] Another objective of the invention is to provide a silver halide photographic material suitable for both modem high intensity exposure and conventional low intensity exposure methods.

[0013] Surprisingly it was found that these objects were achieved by a method of preparing a silverchlorobromide emulsion comprising a nucleation and a growth step in which the presence of a first peptizer having a binding capacity to silver ions of less than 55 milliVolts measured at pH 5 and a second peptizer having a binding capacity to silver ions of at least 55 milliVolts measured at pH 5 are present during at least the growth step.

[0014] Preferably the second peptizer has a binding capacity to silver ions from 75 to 125 milliVolts measured at pH 5, most preferably from 90 to 100 milliVolts

[0015] Preferably said nucleation and growth steps are performed at a pH of 5 or lower in the presence of a first peptizer said peptizer being a polypeptide with at most 5 methionine residues per 1000 aminoacid residues and a second peptizer being a polypeptide with more than 5 methionine residues per 1000 aminoacid residues or wherein said nucleation and growth steps are performed at at a pH higher than 5 in the presence of a first peptizer being a polypeptide with at most 9 methionine plus histidine residues per 1000 aminoacid residues and a second peptizer being a polypeptide with more than 9 methionine plus histidine residues per 1000 aminoacid residues.

[0016] In a further embodiment the method of the invention further comprises the step of precipitating onto the host grains a crystal phase, said crystal phase having a higher bromide content than the host grains. Preferably in this method silver halide grains having a higher silver bromide content than the host grains and having a smaller average grain diameter than the host grains are mixed with said host grains.

[0017] In a further aspect the invention relates to silverchlorobromide emulsions obtainable with the method according to the invention.

[0018] In yet a further aspect the invention relates to photographic material comprising on a support at least one layer comprising a silverchlorobromide emulsion prepared according to or obtainable with the method according to the invention.

Detailed description.

[0019] The present invention is directed to a method for preparing silver halides suitable for fast processing, more specifically to regular shaped non-tabular high chloride silver halide host crystals, more particularly to host crystals on which silver bromide is selectively deposited on the edges and/or corners of said host crystals. It especially relates to silver halide crystals suitable for fast processing. Photographic material that comprises crystals formed with the method according to the invention exhibit excellent high intensity reciprocity law failure and are suitable for high intensity, short time exposure.

[0020] Surprisingly it was found that this could be achieved by preparing a high chloride host crystal on which a high bromide phase is precipitated onto the comers or edges, optimally replacing conventional peptizer when nucleating and growing at a pH of at most 5 by a peptizer being a polypeptide with more than 5 methionine residues per 1000 aminoacid residues or when nucleating and growing at a pH higher than 5 by a peptizer being a polypeptide with more than 9 methionine plus histidine residues per 1000 aminoacid residues, having a binding capacity to silver ions of at least 55 mV at pH 5.0, preferably at least 75 mV at pH 5, most preferably at least 90 mV at pH 5, measured according to the method described in example 1 which in short is as follows:

[0021] Peptizer, for example gelatin, is dissolved in water. Optionally, excess contaminations like salts that may disturb the measurement are removed from the peptizer by, for example, dialysis or (ion)chromatography. After dissolving, silver nitrate solution is added. After equilibration the potential is measured as described in EP 0926543 page 27, line 38-45. As control the potential of a silver nitrate solution in water is measured.

[0022] The potential difference between control and gelatin solution is the binding capacity of the measured gelatin. Any temperature can be applied for the potential measurements.

[0023] Nucleation is defined as the formation of nuclei or silver halide host crystals from an appropriate solution of silver ions and halide ions in the presence of a nucleation peptizer. Growth is defined as increasing the size of the silver halide nuclei formed during nucleation wherein solutions of silver ions and halideions are added to said nuclei under conditions where no new nuclei are formed. Peptizer present during growth can be the same as that present during nucleation or it can be a different peptizer.

[0024] Nucleation and growth peptizers, in this description also referred to as first peptizer or conventional peptizer or reference peptizer, that are used in the state of the art are usually isolated natural gelatins.

[0025] Silver chloride crystals are required for fast development, but have low sensitivity. Additional crystal phases are precipitated onto the silver chloride host crystals to increase the sensitivity of those crystals. These bromide phases are precipitated in the presence of shallow electron traps like iridium for the purpose of maintaining an adequate level of (high intensity) reciprocity law failure. Depositing increasing amounts of silver bromide on the comers or edges increases sensitivity of the crystals accordingly, but reduces the developing speed of the crystal.

[0026] The term maximum density refers to the density under condition where dye formation of a given photographic paper is in principle independent of exposure and therefore limited by developing process parameters, as described in James, Theory of the Photographic Process, 4th edition, Chapter 17-G (also refers to terms sensitivity or gradation/ Log Eb).

[0027] Peptizers that suitably can be applied in the method of the invention are those containing a nitrogen atom, a phosphorus atom, an oxygen atom, or a sulphur atom in the molecule as a coordination atom to a metal, like Ag. Examples of structural elements that contain such coordinating atoms include furan, thiophene, oxazole, isooxazole, thiazole, isothiazole, imidazole, pyrazole, triazole, furazane, pyran, pyridine, pyridazine, pyrimidine, and pyrazine.Compounds having such a structural elements as a fundamental skeleton and a substituent introduced there into are preferred.

[0028] More preferred are peptizers that contain silver-ion binding groups like methionine (or thioether derivates), histidine (or imidazole derivates) or thiol derivates. In particular gelatins comprising said silver-ion binding groups are preferred.

[0029] Most preferred peptizers are gelatins having at least 5 methionine residues per 1000 aminoacid residues and/ or a binding capacity to silver ions of higher than 55 mV. Such a suitable petizer is for instance gelatin from cold-blooded animals like fish. Fish gelatin contains higher amounts of methionine and histidine compared to conventional gelatin used as peptizer, like gelatin from the bones or hide of cattle or pigs. Fish gelatin contains about 12 methionine residues and about 7 histidine residues per 1000 aminoacids. Concentrations may vary between different types of fish or between cold-blooded species. A conventional gelatin like Calf skin gelatin, for example, contains about 4 methionine residues and about 5 histidine residues per 1000 aminoacids.The amino-acid composition of fish gelatin is described in, for example, Advances in Fisheries Technology and Biotechnology; Voight & Botta. Papers from the 34th Atlantic Fisheries Technological Conference and Seafood Biotechnology, Aug-Sept 1989, Technomic Publishing.

[0030] Peptizers are normally de-ionized to reduce impurities like Ca, Mg, Ba, Al, NO3, SO4, Cl - ions). Such impurities can have adverse effects on photographic properties like for instance sensitivity. If necessary the ionic levels can be compensated by adding the required ion to the dispersion solution, but this is normally not preferred.

[0031] Gelatins having the desired binding capacity can be produced synthetically or by recombinant methods similar to those described in for example EP 1014176.

[0032] In case natural peptizers like gelatins or gelatin derivates have too high binding capacity to silver ions of more than 200 mV or even more than 150 mV -at pH higher than 6, the binding capacity can be adjusted to the desired level by oxidation of methionine, as described in U.S. Patent 4,713,323. High binding capacities of over 150 mV can occur at increasing pH where histidine, arginine and lysine can bind silver ions in addition to methionine. Oxidation is normally carried out to reduce the silver ion binding capacity of the peptizer molecules, particularly methionine is affected by oxidation. Several procedures to oxidize peptizers like gelatin are described. Among others Moll described the influence of several oxidizing agents, in Photographic Gelatin, Proceedings of the 5th IAG Conference held in Fribourg, page 181-192, 1988.

[0033] A peptizer that can be suitably applied in the method of the invention has an average molecular weight of at most 150 kiloDalton (kDa). Higher average molecular weights will disturb development and formation of the localized silver bromide phase. An average molecular weight of less than 70 kD is preferred. Most preferred are average molecular weights of less than 30 kD. Too small peptizers of less than about 1 kilodalton (kD) are not preferred, since these adsorb to strongly to silver ions. A more preferred peptizer is more than 5 kD, most preferably more than10 kD. Thus the second peptizer has a molecular weight of less than 150 kD, preferably between 1 kD and 100 kD, more preferably between 5 kD and 80 kD, even more preferably between 10 kD and 50 kD, most preferably between 15 and 30 kD.

It will be evident to a person skilled in the art that the optimal degree of replacement of conventional first peptizer by a second peptizer with high binding capacity to silver ions will vary between silver halide emulsions. The optimisation can be done in two series of experiments, first determining roughly the replacement percentage, then fine-tuning it in a second series. This takes only little effort.

[0034] Silver halide crystals in the emulsion prepared according to the invention are preferably cubic or cubo-octahedral grains substantially having {100} planes. The crystals may be rounded of at the apexes and may have plains of higher order. Also tabular crystals having {100} or {111} major plains as described for example in US 5,830,633 or US 4,463,087 can be used.

[0035] In the present invention cubic crystals are preferred. The silver halide crystals comprise silver chloride, silver bromide, silverchlorobromide or silverchloro(iodo)bromide. It is preferable for fast processing to use silver chloride crystals, or silver chlorobromide crystals with a silver chloride content of at least 95%, more preferably at least 98%.

[0036] The silver halide emulsions prepared with the method of the invention are those containing silver chloride grains having a silver bromide localized phase, said phase preferably formed by epitaxial growth and containing at least 10 mol% of silver bromide, preferably from 10 to 60 mol% and most preferably from 20 to 50 mol%.

[0037] In the method of the invention peptizers are present during the growth step, but can be added before or during the nucleation step. In addition usually peptizers are present and/or may be added during the physical ripening process.

[0038] The peptizer is applied at pH between 2 and 9, preferably between 2 and 5 when the peptizer contains groups which silver-ion binding capacity varies with pH, like histidine, lysine or arginine in gelatin. In such cases applying the peptizer at a pH higher than the iso-electric point of such groups may result in too high binding capacity

[0039] The nucleation temperature can range from ambient or 25°C up to 90°C, preferably from 35°C to 70°C. Below 25°C setting or aggregation of gelatin solution will occur. When only fish gelatin is used, or applied in combination with a conventional peptizer (like lime bone gelatin) nucleation temperatures below 25°C can also be used. Particularly gelatins from cold-blooded animals like fish living in cold water are very useful for nucleation temperatures below 25°C, and as low as about 5°C, depending on the average molecular weight. Such gelatins have lower setting temperatures due to lower hydroxyproline content. A lower nucleation temperature can beneficially be applied to provide more efficient control of the shape of cubic silver chloride.

[0040] The silver bromide localized phase is preferably doped with 10^{-9} to 10^{-2} mol/mol silver of complex ions of metals of Group VIII of the periodic system comprising iridium or rhodium and those exemplified by, but not limited to, EP 1139170 A2 paragraphs 0077 and 0078.

[0041] Preferably the silver halide crystals that are formed have an average size of 0.1 to 2 micrometer, the size being calculated as the number average of the circle equivalent diameter of the projected area of the silver halide grains. The crystal size distribution is preferably monodisperse, having a variation coefficient of less than 20%, more preferably less than 15% more preferably less than 10%.

[0042] Anti-fogging agents or agents stabilizing the silver halide emulsion during production storage or processing can be added, specific examples of which are disclosed in JP 62-215272 A, page 39-72 and EP 0447647 A.

[0043] The silver chlorobromide emulsion prepared according to the method of the invention can be used for making photographic material. The emulsion is applied onto a support and as such forms one of multiple layers of a photographic film. The advantages of the silverchlorobromide emulsion such as excellent high intensity reciprocity law failure while keeping good short time latent image stability in particular come to light when the host crystals that are formed at some moment undergo a sensitization step.

[0044] Spectral sensitization is carried out for the purpose of imparting spectral sensitivity in a desired light wavelength region to the light-sensitive emulsion in each layer of the photographic material of the present invention.

[0045] Spectral sensitizing dyes which are used in the photographic material of the present invention for spectral sensitization of blue, green and red light region include those disclosed by F. M. Harmer, in Heterocyclic Compounds - Cyanine Dyes and Related Compounds, John Wiley & Sons, New York, London (1964). Specific examples of compounds and spectral sensitization processes that are preferably used in the present invention include those described in JP-A-62-215272, from page 22, right upper column to page 38. In addition, the spectral sensitizing dyes described in JP-A-3-123340 are very preferred as red-sensitive spectral sensitizing dyes for silver halide emulsion grains having a high silver chloride content from the viewpoint of stability, adsorption strength and the temperature dependency of exposure, and the like.

[0046] The amount of these spectral sensitizing dyes to be added can be varied in a wide range depending on the occasion, and is preferably in the range of 5×10^{-6} mole to 1.0×10^{-2} mole, more preferably in the range of 1.0×10^{-6} mole to 5.0×10^{-3} mole, per mole of silver halide.

[0047] Silver halide emulsions according to the present invention are generally chemically sensitised. Chemical sensitization can be performed by utilizing a sulphur sensitization, represented by the addition of an unstable sulphur compound, noble metal sensitization represented by gold sensitization, and reduction sensitization, each singly or in combination thereof. Compounds that are preferably used for chemical sensitization include those described in JP-A-62-215272, from page 18, right lower column to page 22, right upper column. Of these chemical sensitization, gold-sensitised silver halide emulsion are particularly preferred, since a change in photographic properties which occurs when scanning exposure to laser beams or the like is conducted, can be further reduced by gold sensitization. In order to conduct gold sensitization, compounds such as chloroauric acid or a salt thereof, gold thiocyanates, gold thiosulfates, and colloidal gold sulphide may be used. The amount of these compounds to be added can be varied in a wide range depending on the occasion, and is generally in the range of 5×10^{-7} mole to 5×10^{-3} mole, preferably in the range of 1.0×10^{-6} mole to 1×10^{-4} mole, per mole of silver halide. In the present invention, gold sensitization may be used in combination with other sensitizing methods, for example, sulphur sensitization, selenium sensitization, tellurium sensitization, reduction sensitization, or noble metal sensitization using a noble metal compound other than gold compounds.

[0048] Thus in a further embodiment the invention relates to a method in which prior to and/or during and/or after the step of precipitating a crystal phase onto the host grains a sensitisation step is performed. Preferably the sensitisation step includes gold sensitisation. It should be noted however, that gold sensitised emulsions suffer less from HIRLF than those that are not gold-sensitised, and thus when gold sensitisation is applied the advantageous effect of the present invention is less prominent compared to for instance absence of a sensitisation step.

[0049] The silver halide photographic light-sensitive material of the present invention can be used for a colour negative film, a graphic arts film, a colour positive film, a colour reversal film, a colour reversal photographic printing paper, a colour photographic printing paper and the like, preferably a colour photographic printing paper.

[0050] The light-sensitive material of the present invention can preferably be used, in addition to the printing system using a general negative printer, in a exposure system like a cathode ray tube (CRT) or in a digital scanning exposure system using high intensity monochromatic light like lasers or light-emitting diodes as described in EP 1139170 A2 0115-0122 or US 5,573,898 column 65 line 43 to column 66 line 36.

[0051] With respect to the processing method of the photographic material of the present invention, processing materials and processing methods, as disclosed in JP-A-2-207250, from page 26, right under column, line 1 to page 34, right upper column, line 9, and JP-A-4-97355, from page 5, left upper column, line 17 to page 18, right under column, line 20, can be preferably applied.

[0052] The silver halide emulsions prepared according to the method of the present invention are preferably applied to a light-sensitive material having rapid processing suitability.

[0053] The term "colour developing time" as used herein refers to a period of time required from the beginning of dipping a light-sensitive material into a colour developing solution until the light-sensitive material is dipped into a blix solution in the subsequent processing step. In the case where a processing is carried out using, for example, an autoprocessor, the colour developing time is the sum total of a time in which a light-sensitive material has been dipped in a colour developing solution (so-called "time in the solution") and a time in which the light-sensitive material has been conveyed in air toward a bleach-fixing bath in the step subsequent to colour development (so-called "time in the air"). Likewise, the term " blix time" as used herein refers to a period of time required from the beginning of dipping a light-sensitive material into a blix solution until the light-sensitive material is dipped into a washing bath or a stabilizing bath in the subsequent processing step. Further, the term "washing or stabilizing time" as used herein refers to a period of time required from the beginning of dipping a light-sensitive material into a washing solution or a stabilizing solution until the end of the dipping toward a drying step (so-called "time in the solution").

[0054] In the present invention, the developing-developing time is preferably 60 sec or less, more preferably from 50 sec to 6 sec, further preferably from 30 sec to 6 sec. Likewise, the blix time is preferably 60 sec or less, more preferably from 50 sec to 6 sec, further preferably from 30 sec to 6 sec. Further, the washing or stabilizing time is preferably 150 sec or less, more preferably from 130 sec to 6 sec.

[0055] Examples of a development method applicable to the photographic material of the present invention after exposure, include a conventional wet system, such as a development method using a developing solution containing an alkali agent and a developing agent, and a development method wherein a developing agent is incorporated in the photographic material and an activator solution, e.g., a developing agent-free alkaline solution is employed for the development, as well as a heat development system using no processing solution. In particular, the activator method using a developing agent-free alkaline solution is preferred over the other methods, because the processing solution contains no developing agent, thereby it enables easy management and handling of the processing solution and reduction in waste disposal load to make for environmental preservation.

[0056] The preferable developing agents or their precursors incorporated in the photographic materials in the case of adopting the activator method include the hydrazine compounds described in, for example, JP-A-8-234388, JP-A-9-152686, JP-A-9-152693, JP-A-9-211814 and JP-A-9-160193.

[0057] Desilvering solution (bleaching/fixing solution), washing solution and stabilizer for use in the present invention can contain known ingredients and can be used in conventional manners. Preferably, those described in Research Disclosure, Item 36544, pp. 536-541 (September 1994), and JP-A-8-234388 can be used in the present invention.

Example 1: Silver ion binding properties of traditional (state of the art) lime bone gelatin compared to fish gelatin.

[0058] Method: 180mg gelatin is weighed and dissolved in 75ml de-ionized water. Optionally the gelatin is subjected to, for example, dialysis or (ion)chromatography to remove excess contaminations like salts that may disturb the measurement and mask the gelatin property as it is when applied in a silver halide emulsion. The gelatin is dissolved at 45°C for 15 minutes. After dissolving 750µl 0.5mM silver nitrate solution is added, under constant mixing. After 15 minutes equilibration the potential is measured as described in EP 0926543 page 27, line 38-45. As control to 75ml de-ionized water 750µl 0.5mM silver nitrate solution is added, under constant mixing. After 15 minutes equilibration the potential is measured.

Table 1:

Ag binding of traditional lime bone gelatin and fish gelatin, ΔmV.				
Gelatins	pH 3.0	pH 5.0	pH 6.0	pH 7.0
reference (state of the art) first peptizer:	*ΔmV*	*ΔmV*	*ΔmV*	*ΔmV*
gelatin 1: lime bone gelatin, non oxidized	25.0	48.2	77.2	109.5
gelatin 2: lime bone gelatin as 1, non oxidized hydrolyzed, average MW 23kDa	24.0	46.2	70.3	108.0
Second peptizer:				
gelatin 3: fish gelatin, non oxidized	55.7	92.0	129.7	199.1
gelatin 4: fish gelatin, hydrolyzed to an average MWof 70kDa	53.0	94.0	129.1	200.9
gelatin 5: fish gelatin, hydrolyzed to an average MWof21kDa	52.7	95.0	129.3	201.1

[0059] The potential difference between the two is the binding capacity of the measured gelatin. Any temperature can be applied for the potential measurements. In this example 35°C was used as measuring temperature, the potential values at 15°C were measured too and were not significantly different compared to the 35°C values. Table 1 gives an overview silver ion binding of conventional first peptizer and second peptizer as used in the method of the invention.

Example 2: Optimized replacement of first peptizer by second peptizer Preparation of reference silver halide emulsion 1-2:

[0060] To a reaction vessel containing 1 litre of a mixture containing 6 weight % de-ionized lime bone gelatin , 838ml de-ionized water and 0.06 molar NaCl, 325ml 1.086M $AgNO_3$ and 160.9ml 2.221M NaCl is added at a temperature of 47°C and a pH of 3.5. The addition flow of the 1.086M $AgNO_3$ is 8.0cc/min and for the 2.21M NaCl 3.8cc/min. In a second addition 1.41 mol of a silvernitrate solution and 1.44 mol of a sodiumchloride solution are added simultaneously with a flow of 22 and 15.5 cc/min respectively. After the additions are completed the growth of the crystals is stopped and excess of ions are removed by a washing step. The average crystal size measured by disk centrifugal photosedimentation is 480nm

[0061] The nucleation and growth temperature can vary depending on the amount and type of peptizer added or replacing the conventional peptizer or state of the art lime bone gelatin. Sensitivity differences of up to 0.05 were not considered to be significant. Excessive amounts of ions were removed in the 2 washing steps. Silver bromide guest crystals are grown epitaxially on the corners of the host crystal and the crystals are subjected optimally to chemical ripening by adding a sulphur-sensitiser and to optimal spectral sensitization, in this case with a green light spectral sensitiser.

[0062] After preparation the emulsion is coated in the third, green sensitive, layer on a laminated paper base using a slide or giesser coating as described in, for example, US6,103,460 column 75-90. The coated and aged samples were exposed on Fuji's Digital minilab Frontier 350 system. Latensification was determined by developing samples after 3 minutes and after 15 seconds after exposure for 0.2 seconds, using 250CMS and 4000 lux.

[0063] After exposure the samples were developed for 45 seconds using Fuji-Hunt CPRA-pro chemistry. The development is followed by 45 seconds bleach fix treatment and finally a 90 seconds washing step was performed. The optical density of the developed samples was measured using an X-rite® 310 optical densitometer

[0064] Silver halide emulsions 103-107 were prepared in the same way as in example 1 except that the conventional peptizer was partly replaced by a second peptizer with high binding capacity see table 2. Coating and processing was performed as described above. The maximum density Dmax of the green-sensitive layer was measured after 10^{-5} seconds exposure. Latensification was determined as described above by calculating the difference in sensitivity between developing samples 3 minutes and developing samples 15 seconds after exposure.

Table 2:

	first peptizer	binding strength (mV, pH 5)	second peptizer	binding strength (mV, pH 5)	ratio second/ first peptizer	sensiti vity (S0.5)	Dmax (magen ta)	latensi fication (3'-15")
1	gelatin 1	48.2	none	92.0	0%	1.313	1.653	0.088

Table 2: (continued)

	first peptizer	binding strength (mV, pH 5)	second peptizer	binding strength (mV, pH 5)	ratio second/ first peptizer	sensiti vity (S0.5)	Dmax (magen ta)	latensi fication (3'-15")
2	gelatin 1	48.2	gelatin 2 comparative	46.2	50%	1.320	1.699	0.080
3	gelatin 1	48.2	gelatin 5 inventive	92.0	2%	1.308	1.7	0.078
4	gelatin 1	48.2	gelatin 5 inventive	92.0	5%	1.299	1.767	0.074
5	gelatin 1	48.2	gelatin 5 inventive	92.0	10%	1.301	1.809	0.058
6	gelatin 1	48.2	gelatin 5 inventive	92.0	13%	1.273	1.828	0.062
7	gelatin 1	48.2	gelatin 5 inventive	92.0	20%	1.134	1.966	0.050

[0065] The applied second peptizer with high silver ion binding capacity, in this example a hydrolyzed fish-skin gelatin with an average molecular weight of 21 kiloDalton, increased maximum density after high intensity, ultra short, exposure (<0.01 seconds) but also improved latensification properties. However, table 2 shows that increasing replacement of the conventional peptizer by fish-skin gelatin results in a decreased sensitivity. It is desirable that the photographic color paper of this invention can be used in both digital and conventional systems. Although the high intensity of laser-exposure and similar techniques diminishes the need for high sensitivity photographic paper, a compromise has to be found for conventionally exposed papers between the beneficial effect of the replacement of conventional low binding capacity peptizer by high bindingcapacity peptizer and the undesired sensitivity decrease. A sensitivity decrease of more than 0.05 as in sample 7 is undesirable for applications using conventional exposure.

[0066] In these examples a 23kD fishskin gelatin is used. To rule out a possible molecular weight effect 50% of the conventional peptizer was replaced by a 23kD conventional peptizer with bindingcapacity comparable to the conventional peptizer. Sample 2 in table 2 shows that this has not the effect of adding a 21 kD fishskin gelatin.

[0067] It will be evident to a person skilled in the art that this optimum varies between different emulsions, where the size and the total number of crystals in the photographic emulsions play a role, as well as the (relative) amount of peptizer added. A latensification of about 0.06 is still acceptable in digital applications so that in this case the optimal replacement is about 13%.

Example 3: Restriction on molecular weight of second peptizer

[0068] Silver halide emulsions were prepared, coated and processed as in example 2, except that the average molecular weight of the fish skin gelatin was varied as indicated in table 3.

[0069] As demonstrated in example 2, reduction of sensitivity when replacing conventional peptizer by a second high binding capacity peptizer like 21kD fish skin gelatin determines the optimum replacement. When adding higher molecular weight fish-skin gelatin has an increasingly worseeffect on sensitivity, and the acceptable replacement-percentage is reduced, as shown in table 3:

Table 3

	first peptizer	second peptizer	optimimum ratio second/ first peptizer	Average MW (kD)	Dmax (magenta)	latensifi cation, (3'-15")
1	gelatin 1	none	not applicable	168.0	1.653	0.088
8	gelatin 1	gelatin 3 inventive	1%	200.0	1.685	0.078

Table 3 (continued)

	first peptizer	second peptizer	optimimum ratio second/ first peptizer	Average MW (kD)	Dmax (magenta)	latensifi cation, (3'-15")
9	gelatin 1	gelatin 4 inventive	5%	70.0	1.921	0.064
7		gelatin 5 inventive	13%	21.0	1.966	0.050

[0070] When conventional peptizer is replaced by increasing amounts of second peptizer the sensitivity is reduced drastically. This effect gets worse if the molecular weight of the second peptizer is increased. Examples 8-9 indicate that the average molecular weight of the second peptizer with high binding capacity preferably does not exceed about 70 kiloDalton. Most preferably the second peptizer has an average molecular weight of about 21 kiloDalton.

Example 4: Application of second peptizer in silver halide with high pH. Preparation of silver halide emulsion:

[0071] To a reaction vessel containing 1 litre of a mixture containing 6 weight % de-ionized lime bone gelatin , 838ml de-ionized water and 0.06 molar NaCl, 325ml 1.086M $AgNO_3$ and 160.9ml 2.221M NaCl is added at a temperature of 45.5°C and a pH of 9.0. The addition flow of the 1.086M $AgNO_3$ is 8.0cc/min and for the 2.21M NaCl 3.8cc/min. In a second addition 1.41 mol of a silvernitrate solution and 1.44 mol of a sodiumchloride solution are added with a flow of 22 and 11.5 cc/min respectively. After the additions are completed the growth of the crystals is stopped and excess of ions are removed by a washing step. The average crystal size measured by disk centrifugal photosedimentation is 550nm.

[0072] The nucleation and growth temperature can vary depending on the amount and type of peptizer added or replacing the conventional peptizer or state of the art lime bone gelatin. Sensitivity differences of at most 0.05 were not considered to be significant. Excessive amounts of ions were removed in the 2 washing steps. Silver bromide guest crystals are grown epitaxially on the corners of the host crystals and the crystals are subjected optimally to chemical ripening by adding a sulphur-sensitiser and to optimal spectral sensitisation, in this case with a red light spectral sensitiser.

[0073] After its preparation, the emulsion is coated in the fifth, red light sensitive, layer on a laminated paper base using a slide or giesser coating as described in , for example, US6,103,460 column 75-90. The coated and aged samples were exposed on Fuji's Digital minilab Frontier 350 system. Latensification was determined as described in previous examples. After exposure the samples were total developed for 45 seconds using Fuji-Hunt CPRA-pro chemistry. The development is followed by 45 seconds bleach fix treatment and finally a 90 seconds washing step was performed. The optical density of the developed samples was measured using an X-rite® 310 optical densitometer. The results are shown in table 4.

Table 4

	first peptizer	binding strenght (mV, pH5)	second peptizer	binding strength (mV, pH5)	ratio second/ first peptizer	Dmax (cyan)	latensifi cation, (3'-15")
10	gelatin 1	48.2	none		0%	2.085	0.096
11	gelatin 1	48.2	gelatin 5 inventive	95.0	1%	2.096	0.091
12	gelatin 1	48.2	gelatin 5 inventive	95.0	3%	2.110	0.067
13	gelatin 1	48.2	gelatin 5 inventive	95.0	7%	2.141	0.063
14	gelatin 1	48.2	gelatin 5 inventive	95.0	10%	2.140	not measured[1]

1) Due to too soft gradation

[0074] Increasing replacement of peptizer with 21 kD fish skin gelatin results in improved high intensity reciprocity law failure as can be seen from the increased cyan Dmax. Also latensification is improved, up to 7% replacement. A replacement of 10% resulted in a too soft gradation. Although the invention can clearly also be beneficially applied in emulsions in which nucleation and/or growth takes place at high pH, it is also illustrated that the optimum replacement depends on the nature of the emulsion.

Example 5: Application of second peptizer in silver halide with gold-sensitisation. Preparation of silver halide emulsion:

[0075] To a reaction vessel containing 1 litre of a 4.8% weight de-ionized lime bone gelatin and 0.045 molar NaCl. pH is adjusted to 3.0 with sulphuric acid. A nucleation step was carried out at 57°C. by adding 24.7ml of a 2.00 M NaCl solution with a flow of 3.4 ml/minute and 30.8 ml of a 2.42 M AgCl with a flow of 4.4ml/minute. In a second addition1.34 mol of a silver nitrate solution and 0.877 mol of a sodium chloride solution were added. Both additions had a start-flow of 4.0ml/minute. The flows were increased during addition with 0.1ml/minute. After the second addition 0.35 mol of a silver nitrate solution was added with a flow of 16.0 ml/minute, simultaneously with 0.24 mol of a sodium chloride solution with a flow of 16.3ml/minute. The nucleation and growth temperature can vary depending on the amount and type of peptizer added or partly replacing the conventional peptizer. The excess of ions was removed in 2 washing steps

[0076] The crystals are subjected optimally to chemical ripening by adding a gold-sensitizer and silver bromide guest crystals are grown epitaxiallyon the corners of the host crystal. Next, the crystals are subjected optimally to spectral sensitization, in this case with a green light spectral sensitizer

[0077] After its preparation, the emulsion is coated in the third, green sensitive, layer on a laminated paper base using a slide or giesser coating as described in , for example, US6,103,460 column 75-90. The coated and aged samples were exposed on Fuji's Digital minilab Frontier 350 system. Latensification was measured as described in previous examples. After exposure the samples were total developed for 45 seconds using Fuji-Hunt CPRA-pro chemistry. The development is followed by 45 seconds bleach fix treatment and finally a 90 seconds washing step was performed. The optical density of the developed samples was measured using an X-rite® 310 optical densitometer. The results are shown in table 5.

Table 5

	first gelatin	binding strength (mV, pH5)	second gelatin	binding strength (mV, pH5)	ratio second/first gelatin	Sensiti vity (S0.5)	Gradation (Log Eb, cyan)	latensific ation, (3'-15")
15	gelatin 1	48.2	none	95.0	0%	1.519	0.627	0.02
16	gelatin 1	48.2	gelatin 5	95.0	1%	1.578	0.613	0.03
17	gelatin 1	48.2	gelatin 5	95.0	3%	1.552	0.603	0.001
18	gelatin 1	48.2	gelatin 5	95.0	7%	1.514	0.638	0.005

[0078] For this emulsion the maximum density was not affected by high intensity exposure, but the emulsion is clearly getting softer gradation (measured in the shoulder-part of the sensito-curve) which is not observed at conventional exposure times. In this case the optimum is determined by the gradation-loss rather than the loss in sensitivity, and is about 4-5%.

Claims

1. A method of preparing a silver chlorobromide emulsion comprising a nucleation and a growth step in which a first peptizer having a binding capacity to silver ions of less than 55 milliVolts measured at pH 5 and a second peptizer having a binding capacity to silver ions of at least 55 milliVolts measured at pH 5 are present during at least the growth step.

2. A method according to claim 1 wherein the second peptizer has a binding capacity to silver ions from 75 to 125 milliVolts measured at pH 5, preferably from 90 to 100 milliVolts

3. A method according to claim 1 or 2 wherein said nucleation and growth steps are performed
   at a pH of 5 or lower in the presence of a first peptizer said peptizer being a polypeptide with at most 5 methionine residues per 1000 aminoacid residues and a second peptizer being a polypeptide with more than 5

methionine residues per 1000 aminoacid residues, or
wherein said nucleation and growth steps are performed

at at a pH higher than 5 in the presence of a first peptizer being a polypeptide with at most 9 methionine plus histidine residues per 1000 aminoacid residues and a second peptizer being a polypeptide with more than 9 methionine plus histidine residues per 1000 aminoacid residues.

4. A method of preparing a silver chlorobromide emulsion comprising a nucleation and growth step wherein said steps are performed

at a pH of 5 or lower in the presence of a first peptizer said peptizer being a polypeptide with at most 5 methionine residues per 1000 aminoacid residues and a second peptizer being a polypeptide with more than 5 methionine residues per 1000 aminoacid residues, or
wherein said nucleation and growth steps are performed

at at a pH higher than 5 in the presence of a first peptizer being a polypeptide with at most 9 methionine plus histidine residues per 1000 aminoacid residues and a second peptizer being a polypeptide with more than 9 methionine plus histidine residues per 1000 aminoacid residues.

5. Method according to preceding claims in which the second peptizer is a polypeptide with 10 to 15 methionine residues per 1000 aminoacid residues or 15 to 25 methionine plus histidine residues per 1000 aminoacid residues.

6. Method according to the preceding claims in which the molecular weight of the second peptizer is less than 150 kD, preferably between 1 kD and 100 kD, more preferably between 5 kD and 80 kD, even more preferably between 10 kD and 50 kD, most preferably between 15 and 30 kD.

7. Method according to any of the preceding claims in which of the total amount of peptizer at most 20% by weight second peptizer with molecular weight of less than 50 kD is present or at most 15% by weight second peptizer with molecular weight of 50 kD to 80 kD is present or at most 5% by weight second peptizer with molecular weight of more than 80 kD is present.

8. Method according to any of the preceding claims in which the second peptizer is a gelatin from cold-blooded animals, preferably a fish gelatin, most preferably from fish skin gelatin.

9. Method according to any of the preceding claims which further comprises the step of precipitating onto the host grains a crystal phase, said crystal phase having a higher bromide content than the host grains.

10. Method according to claim 9 in which silver halide grains having a higher silver bromide content than the host grains and having a smaller average grain diameter than the host grains are mixed with said host grains.

11. Method according to any of the preceding claims in which prior to and/or during and/or after the step of precipitating a crystal phase onto the host grains a sensitization step is performed.

12. Method according to claim 11 in which the sensitization step includes gold sensitization.

13. Silver chlorobromide emulsion obtainable with the method according to any of the preceding claims

14. Photographic material comprising on a support at least one layer comprising a silverchlorobromide emulsion according to claim 13

European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number
EP 02 07 7820

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.7)
X	US 5 888 718 A (MASKASKY JOE E ET AL) 30 March 1999 (1999-03-30)	3-8	G03C1/047 G03C1/015
Y	* column 3, line 28 - line 50 * * column 4, line 52 - column 6, line 61; table 2 * * column 7, line 57 - line 62 * * column 20, line 36 - line 40; claims 1,9,10; example 11 * ---	9-14	
Y	EP 0 843 208 A (AGFA GEVAERT NV) 20 May 1998 (1998-05-20) * claim 1 * ---	3-14	
Y	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 02, 29 February 1996 (1996-02-29) & JP 07 287334 A (MITSUBISHI PAPER MILLS LTD), 31 October 1995 (1995-10-31) * paragraphs ‘0022!-‘0024!,‘0040!-‘0045!; claims * --- -/--	3-14	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

G03C

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 November 2002	Philosoph, L

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
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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

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INCOMPLETE SEARCH SHEET C

Application Number
EP 02 07 7820

Claim(s) searched completely:
3-14

Claim(s) not searched:
1,2

Reason for the limitation of the search:

Present claims 1 and 2 relate to a method defined (inter alia) by reference to the following parameter:

P = BINDING CAPACITY TO SILVER IONS

The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 84 EPC. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to claims 3-14.

However, this parameter has been searched as such.

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Application Number
EP 02 07 7820

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.7)
Y	DATABASE WPI Section Ch, Week 199601 Derwent Publications Ltd., London, GB; Class G06, AN 1996-007499 XP002222436 & JP 07 287334 A (MITSUBISHI PAPER MILLS LTD), 31 October 1995 (1995-10-31) * abstract * ---	3-14	
D,Y	EP 0 750 220 A (EASTMAN KODAK CO) 27 December 1996 (1996-12-27) * page 5, line 21 - page 6, line 11; claims; figure 1 * -----	9-14	
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EPO FORM 1503 03.82 (P04C10)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 02 07 7820

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82