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(54) Process for the preparation of a photographic tabular emulsion rich in chloride

(57) A process is disclosed for the preparation of a photographic silver halide emulsion comprising one or more precipitation steps in a reaction vessel, said emulsion comprising tabular grains, containing at least 50 mole % of chloride, wherein at least 50 % of the total projected area of all grains is provided by said tabular grains, and wherein said tabular grains exhibit an average aspect ratio of at least 5, an average thickness of at most 0.5 µm, and an average diameter of at least 0.6 µm, characterized in that during said one or more precipitation steps a gelatin binder is present in said reaction vessel which is substantially free of calcium ions.

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Description

1. Field of the invention.

The present invention deals with a photographic emulsion comprising tabular silver halide grains rich in chloride with improved sensitometric properties and to a photographic material containing such an emulsion.

2. Background of the invention.

High aspect ratio tabular grains exhibit several pronounced photographic advantages. 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.

An emulsion is generally understood to be a "tabular grain emulsion" when tabular grains account for at least 50 percent of total grain projected area. A grain is generally considered to be a tabular grain when the ratio of its equivalent circular diameter to its thickness is at least 2. The equivalent circular diameter of a grain is the diameter of a circle having an area equal to the projected area of the grain.

The early patent disclosures on high aspect tabular grains, e.g. US 4,434,226, US 4,439,520, US 4,425,425, US 4,425,426, US 4,433,048 and Research Disclosure, Vol. 225, Jan. 1983. Item 22534, are concerned with high sensitive silver bromide or silver iodobromide emulsions. However in a lot of photographic applications high sensitivity is of less importance. In these cases the use of chloride rich emulsions is advantageous thanks to their higher development and fixing rates. Typical examples include graphic arts contact materials, duplicating materials, hard-copy materials, diffusion transfer reversal materials and black-and-white or color print materials. So it would be interesting to try to combine the advantages of chloride rich emulsions with the advantages of tabular grain structure.

Tabular silver halide grains rich in chloride can show a (111) crystal habit of their major parallel faces or they can show a (100) crystal habit of their major parallel faces. In earlier disclosures most attention was devoted to the preparation of (111) chloride rich tabular grains. So Maskasky US 4,400,463 describes the preparation of a new crystallographic form of tabular silver halide grains rich in chloride by performing the precipitation in the presence of a special peptizer having a thioether linkage and an aminoazaindene growth modifier. Maskasky US 4,713,323 discloses the preparation of thin (111) tabular grains by a precipitation technique wherein oxidized gelatin is used. Tufano US 4,804,621 describes a process for preparing chloride rich (111) tabular grains in the presence of aminoazapyridine growth modifiers. EP 0 481 133 describes the presence of adenine-like compounds in the preparation of chloride rich (111) tabular grains using conventional gelatin, and Maskasky US 5,183,732 discloses similar compounds. Maskasky further describes triaminopyrimidines in US 5,185,239, xanthine derivatives in US 5,178,998, and other heterocyclic compounds in US 5,178,997, all as growth modifiers in the preparation of chloride rich (111) tabular emulsions.

The first publications on tabular grains bounded by (100) parallel major faces concerned silver iodobromide emulsions. Bogg U.S. Pat. No. 4,063,951 and Mignot U.S. Pat. No. 4,386,156 were the most important publications.

In EP 0 534 395 Brust et al. disclose the first chloride rich tabular emulsion and a process for preparing it wherein the tabular grain fraction showing (100) major faces is significant. Further improvements and variations on the teachings of tabular (100) emulsions rich in chloride were described in US 5,292,632, EP 0 569 971, US 5,275,930, EP 0 616 255, US 5,264,337, US 5,310,635, EP 0 617 317, EP 0 617 318, EP 0 617 320. EP 0 617 321, EP 0 617 325, WO 94/22051, WO 94/22054, EP 0 618 492, EP 0 618 493, US 5,314,798, US 5,356,764 and EP 0 653 659.

In conventional photographic materials for radiographic recording high-sensitive silver (iodo)bromide tabular emulsions are currently used. However in view of recent trends to rapid processing it would be desirable to use silver chloride emulsions for their faster developability. In this case, due to the high sensitivity required, silver chloride tabular emulsions with high circular equivalent diameter and high aspect ratio are indispensable hitherto. However, such emulsions show the drawback of too a low covering power, being the ratio of developed density to silver coverage.

The present invention extends the teachings on tabular emulsions rich in chloride.

It is an object of the present invention to provide a photographic material which contains tabular emulsion grains rich in chloride with improved sensitivity in relation to their crystallographic dimensions and with sufficient covering power.

It is a further object of the present invention to provide a photographic material which is suitable for use as radiographic recording material and suitable for rapid processing.

Other objects of the invention will become clear from the description hereinafter.

3. Summary of the invention.

The objects of the present invention are realized by providing a process for the preparation of a photographic emulsion comprising one or more precipitation steps in a reaction vessel, said emulsion comprising tabular grains, containing at least 50 mole % of chloride, wherein at least 50 % of the total projected area of all grains is provided by said tabular grains, and wherein said tabular grains exhibit an average aspect ratio of at least 5, an average thickness of at most 0.5 µm, and an average diameter of at least 0.6 µm, characterized in that during said one or more precipitation steps a gelatin binder is present in said reaction vessel which is substantially free of calcium ions.

In a preferred embodiment the tabular emulsion grains prepared according to the process of the invention contain at least 90 % of chloride, occupy at least 80 % of the total projected area, show an aspect ratio between 8 and 16 and have a thickness of at most 0.2 µm. In a most preferred embodiment the tabular emulsion is a silver iodochloride emulsion containing substantially no bromide.

In a most preferred embodiment the substantially calcium free gelatin is at the same time an oxidized gelatin having a methionine content of less than 30 µmol/g.

4. Detailed description of the invention.

The calcium content of most commercial high-quality inert gelatins is about 0.4 % or about 100 mmol/kg. This figure is the end result of the preparation process of inert gelatin. The basis for a high-quality gelatin preferably consists of pure, degreased hard cattle bones. In a first phase of preparation the bones are treated with acid in order to remove calcium and magnesium phosphates. This is followed by an alkaline hydrolysis, mostly by means of calcium hydroxide, of the residual collagen resulting in gelatin. At the low pH used to remove the phosphates the calcium ions, bound to specific amino acids of the polypeptide, exchange with protons. During the alkaline hydrolysis with calcium hydroxide the polypeptide again takes up calcium ions upto saturation. After diafiltration the non-washable calcium concentration is about 0.5 % or 125 mmol/kg. When slightly acidifying during washing the calcium content can be reduced to about 0.4 % or 100 mmol/kg. These and other data can be found in the scientific publication "Influence of Calcium on the Physical properties of Gelatin Solutions and on Symplex Formation with Macromolecular Polyanions" by B.H. Tavernier, J. Phot. Sci., Vol. 40, (1992), p. 168-173. The author reached the conclusion that complex-bound calcium ions strongly decrease the electric potential carried by gelatin. The influence of calcium ions on physical characteristics such as viscosity was found to be not significant.

Calcium free gelatin is obtained by cation exchange by means of an ion exchange resin, preferably a so-called mixed-bed resin. We define substantially calcium free gelatin as gelatin with a calcium content below 40 ppm which is about the analytical detection limit.

The patent references on calcium free or calcium poor gelatins are rather scarce.

In unexamined Japanese patent publication JP-A 05-173278 a colour negative material is described hardened with a vinylsulphonyl hardener type and containing a calcium poor gelatin.

In JP-A 04-321026 a black-and-white multicontrast material is disclosed using a specific calcium poor gelatin.

In JP-A- 02-300745 a specific AgX material is described comprising gelatin with a calcium content of less than 100 ppm.

It was very surprising to find that the mere use of Ca^{++} free gelatin as binder during the preparation of tabular grains rich in chloride as defined above resulted on such a pronounced effect on the obtained crystallographic and sensitometric properties. More tabular grains are formed that are smaller on the average but nevertheless show an excellent sensitivity.

Moreover, the effect on sensitivity is enhanced in a cumulative way, as will be illustrated by the examples furtheron, by using oxidized gelatin. According to Maskasky US 4,713,323, cited above, we define oxidized gelatin as a gelatin having a methionine content of less than 30 µmol/g. Gelatin can be oxidized by means of e.g. hydrogen peroxide. A publication on the determination of methionine and its oxides in gelatin can be found in J. Phot. Sci., Vol. 41, (1993), p. 172-175, by S. Tani and T. Tani.

Although the emulsion precipitation can be principally performed by one double jet step it is preferred to perform a sequence of a nucleation step, at least one physical ripening step, and at least one growth step. Of the total silver halide preferably 0.5 % to 5.0 % is precipitated during said nucleation step which consists preferably of an approximately equimolecular addition of silver and halide salts. The rest of the silver and halide salts is added during one or more consecutive double jet growth steps. The different steps of the precipitation can be alternated by physical ripening steps. 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. These flow rates can be monitored by e.g. magnetic valves. During the growth step(s) the pAg is preferably maintained at a constant value corresponding to a silver potential preferably about 100 milli-Volt measured by a silver versus an

Ag/AgCl Ingold electrode. The pH is preferably established at a value of at least 4.0, most preferably around 6.0.

Before and during the formation of the silver halide grains it is common practice to establish a gelatin concentration of from about 0.05 % to 5.0 % by weight in the dispersion medium. This gelatin is calcium free according to the invention. Additional gelatin is added in a later stage of the emulsion preparation, e.g. after washing, to establish optimal coating conditions and/or to establish the required thickness of the coated emulsion layer. This gelatin can be conventional calcium containing non-oxidized gelatin. Preferably a gelatin / silver halide ratio ranging from 0.3 to 1.0 is then obtained, wherein silver halide is expressed as silver nitrate.

In a preferred embodiment the chloride rich tabular grains prepared in accordance with the present invention show a (111) crystal habit. In this case a crystal habit modifier is present during the emulsion preparation. Such a modifier can be chosen from the appropriate references cited in the Background section. In a preferred embodiment this crystal habit modifier is a 2-hydroaminoazine, most preferably an aminoazaindene compound. In a most preferred embodiment this aminoazaindene compound is adenine.

The habit modifier used in connection with the present invention can be added at any stage of the silver halide precipitation procedure e.g. before the start of the precipitation, during the nucleation step, during a physical ripening stage or during one or more of the growth steps. The substance can be added to the dispersion medium itself as a solid or as a predissolved aqueous solution; alternatively the substance can be dissolved in one or more of the solutions which are entered into the dispersion medium, e.g. in one or more of the halide or silver salt solutions.

After completion of the precipitation a wash technique in order to remove the excess of soluble salts is applied. Any conventional wash technique can be used e.g. washing with several water portions after flocculation by an inorganic salt or by a polymeric flocculating agent like polystyrene sulphonic acid. In a preferred embodiment ultrafiltration is used as wash technique.

The emulsions containing tabular chloride rich silver halide grains 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 gold-selenium ripeners, or gold-sulphur-selenium 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 silver halide 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. In the preferred embodiment wherein the tabular emulsion is a chloroiodide emulsion the spectral sensitizers are preferably added even before the redispersion step.

The scope of the present invention further encompasses a photographic material prepared according to the process described. In a preferred embodiment this photographic material is a radiographic recording material.

This 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.

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 silver halide emulsion layer(s) of the photographic material 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-bensotriazole), 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.

The gelatin binder of the photographic materials under consideration 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 or methylenebisvinylsulphon, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methyloldimethylhydantoin, 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 European Patent Application No 90.201850.6

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.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US 3,038,805 - 4,038,075 - 4,292,400.

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.

Suitable additives for improving the dimensional stability of the photographic element are e.g. dispersions of a water-soluble or hardly soluble synthetic polymer e.g. polymers of alkyl(meth)acrylates, alkoxy(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, Alpha-Beta-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.

Suitable UV-absorbers are e.g. aryl-substituted benzotriazole compounds as described in US 3,533,794, 4-thiazolidone compounds as described in US 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US 3,705,805 and 3,707,375, butadiene compounds as described in US 4,045,229, and benzoxazole compounds as described in US 3,700,455. UV-absorbers are especially useful in colour recording materials where they prevent the fading by light of the colour images formed after processing.

In the protective layer spacing agents can be present of which, in general, the average particle size is comprised between 0.2 and 10 micron. Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents can be made e.g. of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been described in US 4,614,708.

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 and DE 2,453,217. 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 α-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, polyvinylacetal) film, polystyrene film, polyethylene terephthalate film, polycarbonate film, polyvinylchloride film or poly-α-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 a tabular emulsion 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 replenishment of the processing solutions.

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

EXAMPLES

- Preparation of comparative and invention emulsions

<u>Emulsion A</u> (tabular silver chloride emulsion, comparative emulsion, low degree of gelatin oxidation)

The following solutions were prepared :

- 2.9 l of a dispersion medium (C) containing 0.236 moles of sodium chloride, 75 g of conventional calcium containing inert gelatin containing 6700 ppm methionine, corresponding to 45 µmol/g, and 360 mg of adenine; the temperature was established at 45 °C and the pH was adjusted to 6;
- a 2.94 molar silver nitrate solution (A);
- a solution 2.923 molar of sodium chloride, 0.0147 molar of potassium iodide and containing 420 mg/l of adenine (B1);
- a solution 0.59 molar of potassiumiodide (B2);

A nucleation step was performed by introducing solution A and solution B1 simultaneously in dispersion medium C both at a flow rate of 60 ml/min during 30 seconds. After a physical ripening time of 20 min during which the temperature was raised to 70 °C, a growth step was performed by introducing by a double jet during 29 minutes solution A starting at a flow rate of 5 ml/min and linearly increasing the flow rate to an end value of 13.7 ml/min, and solution B1 at an increasing flow rate as to maintain a constant mV-value, measured by a silver electrode versus an Ag/AgCl Ingold Reference Electrode, of + 108 mV. This growth step was followed by a second growth step where by a double jet during 16 minutes solution A was introduced into the dispersion medium at a flow rate of 5 ml/min and solution B1 at a varying flow rate as to increase the mV-value, measured by a silver electrode versus a Ag/AgCl Ingold Reference Electrode, up to + 135 mV. A third growth step was performed by introducing by a double jet during 50 minutes solution A starting at a flow rate of 5 ml/min and linearly increasing the flow rate to an end value of 20 ml/min, and solution B1 at an increasing flow rate as to maintain a constant mV-value, measured by a silver electrode versus a Ag/AgCl Ingold Reference Electrode, of + 135 mV.

Six minutes later an iodide conversion was performed by introducing solution B2 in the the dispersion medium at a flow rate of 20 ml/min during 2 minutes.

After the precipitation and after the addition of 28 ml of polystyrene sulphonic acid, the pH value of the said dispersing medium was adjusted to a value of 3.0 with sulphuric acid, and the emulsion was cooled down to room temperature. The obtained flocculate was decanted and washed three times with an amount of 4 l of demineralized water in order to remove the soluble salts present.

The thus obtained silver chloride tabular emulsion showed the grain characteristics as illustrated in Table 1 (see furtheron). The average diameter d_{EM}, average thickness t, average aspect ratio AR were obtained from electron microscopic photographs: the diameter of the grain was defined as the diameter of the circle having an area equal to the projected area of the grain as viewed in said photographs. Moreover the average sphere equivalent diameter d_M obtained from the measurement of electric reduction currents obtained by reduction of a silver halide grain with a microscopically fine electrode is given: the sphere equivalent diameter was defined as the diameter of a hypothetical spherical grain with the same volume as the corresponding tabular grain.

<u>Emulsion B</u> (tabular silver chloride emulsion, comparative emulsion, high degree of gelatin oxidation)

For the preparation of emulsion B highly oxidized gelatine was used compared to emulsion A. The gelatine contained only 1074 ppm of methionine. The precipitation was performed exactly in the same way as for emulsion A. Grain characteristics are summarized in Table 1.

Emulsions C (tabular silver chloride emulsion, inventive emulsion, low degree of gelatin oxidation)

For the preparation of emulsion C Ca^{2+}-free gelatine was used. In this case non-oxidized gelatine with high content (6155 ppm) of methionine was used. The precipitation was performed exactly in the same way as for emulsion A. Grain characteristics are summarized in Table 1.

Emulsions D (tabular silver chloride emulsion, inventive emulsion, high degree of gelatin oxidation)

For the preparation of emulsion D highly oxidized Ca^{2+}-free gelatine was used compared to emulsion A In this case gelatine with only 1163 ppm methionine was used. The precipitation was done exactly as to precipitate emulsion A. Grain characteristics are summarized in Table 1.

- crystallographic and photographic properties

TABLE 1

Emulsion	ppm methionine	Ca^{++} free	d_{EM} (µm)	t (µm)	AR	d_M (µm)
A (comp. AgCl(I))	6700	no	2.06	0.10	20	0.87
B (comp. AgCl(I))	1074	no	1.31	0.10	13	0.64
C (inv. AgCl(I))	6155	yes	1.49	0.11	14	0.70
D (inv. AgCl(I))	1163	yes	1.38	0.10	14	0.66

From Table 1 it can be concluded that nor the oxidation degree nor the Ca-content has an influence on the thickness of the grain. High oxidation grades improve production of twin planes since smaller grains with equal thickness are produced (compare A to B). When the gelatine is made Ca^{2+} free the influence of the oxidation degree is reduced drastically so that also for high amounts of methionine lots of twinning occurs (compare C to D).

After the desalting step and during the redispersion of the emulsions 0.85 mmole per mole of silver was added of a green sensitizing dye. Further an amount of 75 g of conventional Ca^{2+} containing non-oxidized inert gelatin was added so that the final weight ratio of gelatin to silver halide (expressed as silver nitrate) was 0.3.

Before the start of the chemical ripening the mV-value of every emulsion was adjusted to +158 mV with sodium chloride and the pH-value was set at 5.5 with sodium hydroxide. The amounts of the chemical ripening agents were adapted to the crystal size of the emulsions.

Chemical ripening agents were gold thiocyanate, sodium thiosulphate as a source of sulphur and toluene thiosulphonic acid was used as predigestion agent. The amounts of each chemical ripening were optimized in order to obtain an optimal fog-sensitivity relationship after 4 hours at 57°C.

Before coating each emulsion was stabilized with 1-p-carboxyphenyl-5-mercaptotetrazole and after addition of conventional coating additives the solutions were coated simultaneously together with a protective layer containing 1.3 g gelatine per m^2 per side on both sides of a polyethylene terephthalate film support having a thickness of 175 µm. The resulting photographic material contained at each side an amount of silver halide corresponding to 3.6 grams of $AgNO_3$ per m^2 and an amount of gelatin corresponding to 3.12 g/m^2.

Samples of these coatings were exposed with green light (through a filter having maximal transmittance at 545 nm) for 0.1 seconds using a continuous wedge, and were processed during a 90 seconds cycle. The processing occurred in a glutaraldehyde containing hydroquinone/1-phenyl-3-pyrazolidinone developer marketed by Agfa-Gevaert N.V. under the trade name G138 having a high activity.

The density as a function of the light dose was measured and therefrom were determined the following parameters:

- fog level F, expressed in 1/thousands of density (with an accuracy of 0.001 density),
- the relative speed S at a density of 1 above fog (an increase of the said speed with a factor of 2 gives a speed value that is 0.30 lower as the relation is logarithmic and as less light is needed to get the desired density),
- covering power CP : the maximum density D_{max} per gram coated silver.

TABLE 2

Emulsion	ppm methion.	Ca^{++-} free	F	S	CP
A (comp. AgCl(I))	6700	no	23	2.08	0.46
B (comp. AgCl(I))	1074	no	34	1.81	0.48
C (inv. AgCl(I))	6155	yes	28	1.77	0.44
D (inv. AgCl(I))	1163	yes	43	1.56	0.45

From Table 2 it can be concluded that the sensitivity increases whzen oxidized gelatin is used (compare A and B). By using gelatin that is Ca^{2+} free the sensitivity is increased even more drastically for the same oxidation degree (compare A with C and B with D). Also it can be concluded that both increases are cumulative. This means that also with Ca^{2+} free gelatine the influence of the oxidation degree stands (compare C and D). Also it can be concluded that no influence is found on the fog nor on the covering power.

Claims

1. Process for the preparation of a photographic silver halide emulsion comprising one or more precipitation steps in a reaction vessel, said emulsion comprising tabular grains, containing at least 50 mole % of chloride, wherein at least 50 % of the total projected area of all grains is provided by said tabular grains, and wherein said tabular grains exhibit an average aspect ratio of at least 5, an average thickness of at most 0.5 µm, and an average diameter of at least 0.6 µm, characterized in that during said one or more precipitation steps a gelatin binder is present in said reaction vessel which is substantially free of calcium ions.

2. Process according to claim 1 wherein said tabular grain emulsion contains at least 90 mole % of chloride.

3. Process according to claim 1 or 2 wherein at least 80 % of the total projected area of all grains is provided by said tabular grains.

4. Process according to any of claims 1 to 3 wherein the aspect ratio of said tabular grains is comprised between 8 and 16.

5. Process according to any of claims 1 to 4 wherein the average thickness of said tabular grains is at most 0.2 µm.

6. Process according to any of claims 1 to 5 wherein the parallel major faces of said tabular grains show a (111) crystal habit.

7. Process according to any of claims 1 to 6 wherein said tabular emulsion is a silver iodochloride emulsion.

8. Process according to any of claims 1 to 7 wherein said gelatin substantially free of calcium is also an oxidized gelatin having a methionine content of at most 30 µmol/g.

9. Photographic material comprising a photographic silver halide emulsion prepared according to any of the preceding claims.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 1371

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.6)
X	EP 0 423 840 A (EASTMAN KODAK COMPANY) * figures; examples * ---	1-9	G03C1/005 G03C1/047
X	US 5 061 617 A (J.E.MASKASKY) * figures; examples * ---	1-9	
X	EP 0 645 670 A (FUJI PHOTO FILM CO., LTD.) * example 1 * -----	1-5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 December 1996	Buscha, A

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
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