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(54) **Sensitised silver halide emulsion crystals having colloidal silica as a sole protective colloid during precipitation**

(57) A method is disclosed of preparing a light-sensitive silver halide emulsion comprising the steps of:

- precipitating silver halide by means of a double-jet or a triple-jet technique in a reaction medium comprising colloidal silica as a protective colloid in the absence of any polymeric compound capable of forming hydrogen bridges with colloidal silica but in the presence of one or more onium compounds, said colloidal silica having an average particle diameter from 0.003 μm to 0.30 μm , the ratio by weight of onium compound(s) to silica being between 0.03 and 0.3 at every moment during precipitation and the ratio by weight of silica to silver halide, expressed as an equivalent amount of silver nitrate, being from 0.01 to 0.3 at the end of precipitation;
- desalting the reaction medium;
- redispersing the silver halide; and
- chemically ripening the said silver halide in the presence of an onium precursor compound together with a combination of compounds in order to generate sensitisation specks comprising silver, gold and selenium or silver, gold, selenium and sulphur.

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Description

1. Field of the invention.

5 This invention relates to a method of preparing light-sensitive emulsions having sensitised silver halide crystals with colloidal silica as a protective colloid and to materials coated with layers containing the said emulsions.

2. Background of the invention.

10 Highly light-sensitive silver halide crystals having a cubic or a tabular habit are known to be very sensitive to pressure sensitisation, a phenomenon which is known as "pressure sensitivity" which may appear as pressure marks, pressure sensitisation or desensitisation, wherein both the protective colloid and the coated matrix have to dissipate the energy developed by the pressure force when the coated layer is dried and deformed afterwards in packaging, before and after exposure and by processing. In the dry state pressure sensitisation or desensitisation may occur.

15 Moreover a phenomenon which makes the problem become worse is the use of thin coated layers by coating lower amounts of binder e.g. for rapid processing applications.

A solution therefore has been described for tabular grains in EP-A 0 677 773, wherein a method has been described for preparing a light-sensitive silver halide emulsion comprising tabular grains containing colloidal silica sol as a protective colloid, said tabular grains having specific morphological characteristics as an average grain thickness
20 of up to 0.3 μm , an average aspect ratio of more than 12:1, a total projective area of the said tabular grains of at least 50 % and a coverage degree by silica sol particles within the range from 50 to 2000 % and wherein the said method comprises as characteristic steps precipitation in a reaction medium of silver halide by means of a double-jet or triple-jet technique applied to aqueous solutions of silver nitrate and halide salts in colloidal silica having an average particle size in the range from 0.003 μm to 0.30 μm as a protective colloid, in the presence of at least one onium compound
25 (except for NH_4^+ as an ammonium compound), but in the absence of gelatin, wherein a ratio by weight of said colloidal silica to said onium compound(s) is between 3 and 400, and adjustment of a ratio by weight of colloidal silica sol to an amount of silver halide, expressed as an equivalent amount of silver nitrate, to a value of at least 0.03 at every moment throughout precipitation in a reaction vessel.

Otherwise a method for preparing regular silica silver halide light-sensitive emulsion crystals and the corresponding
30 regular emulsions, in a reproducible and perfectly predictable way, in small laboratory vessels as well as in large vessel in production units to provide a high and reproducible sensitivity and gradation without dye stain and pressure marks in rapid processing applications has been disclosed in EP-A 0 649 051.

About the same characteristics in the preparation method have been disclosed therein taking into account in addition the step of controlling the nucleation and growth steps by means of variable flow rate(s) of the aqueous solutions
35 of silver nitrate and halide salts and/or by means of constant pAg-values during the said steps in the vessel in order to determine the number of nuclei quantitatively in the nucleation step and to avoid renucleation in the growth step.

In a preferred embodiment therein emulsions having regular or tabular grains are further made ready for coating by addition to the emulsion of an amount of hydrogen-bridge forming polymer and/or silica in such an amount that the ratio of hydrogen bridge-forming polymer to silver halide expressed as silver nitrate is comprised between 0.05 and 0.40 and
40 the ratio of silica to silver halide expressed as silver nitrate is comprised between 0.03 and 0.30.

Since adsorption of the colloidal silica used as a protective colloid occurs at the crystal surface, development characteristics, especially in rapid processing cycles, are further strongly influenced by the said protective colloid.

Gelatin is well-known as the most commonly used protective colloid. It has the characteristics of a thermoreversible polymer, showing a sufficient gel strength after coating, but more important is its stabilising function of silver halide
45 nuclei, growing silver halide crystals and although adsorbed to the said crystals permitting chemical ripening and spectral sensitisation without having restraining properties thereupon. For emulsion crystals having colloidal silica sol as a sole protective colloid during precipitation however in order to get the required sensitometric characteristics, especially high speed, suitable gradation and low fog, it is of utmost importance to create optimal chemical and spectral sensitisation circumstances, taking into account the preferred ratios of colloidal silica to onium compound (used as a co-stabiliser) and colloidal silica to silver coated mentioned hereinbefore in both published EP-Applications.
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3. Objects of the invention.

Therefore it is an object of the present invention to get chemically and, optionally, spectrally sensitised silver halide
55 emulsion crystals having colloidal silica as a sole protective colloid during precipitation, said crystals after having been coated into photographic silver halide light-sensitive emulsion layers showing improved sensitometric characteristics, especially sensitivity (speed), without negatively influencing properties like e.g. pressure sensitivity and dye stain.

4. Summary of the invention.

The objects of this invention have been attained by providing a method of preparing a light-sensitive silver halide emulsion comprising the steps of:

- precipitating silver halide by means of a double-jet or a triple-jet technique in a reaction medium comprising colloidal silica as a protective colloid in the absence of any polymeric compound capable of forming hydrogen bridges with colloidal silica but in the presence of one or more onium compounds, said colloidal silica having an average particle diameter from 0.003 μm to 0.30 μm , the ratio by weight of onium compound(s) to silica being between 0.03 and 0.3 at every moment during precipitation and the ratio by weight of silica to silver halide, expressed as an equivalent amount of silver nitrate, being from 0.01 to 0.3 at the end of precipitation;
- desalting the reaction medium;
- redispersing the silver halide; and
- chemically ripening the said silver halide in the presence of an onium precursor compound together with a combination of compounds in order to generate sensitisation specks comprising silver, gold and selenium or silver, gold, selenium and sulphur.

5. Detailed description.

As onium compounds acting as effective colloidal stabilisers of silica sol, provided that according to this invention an appropriate amount is added to the reaction vessel versus the amount of silica present therein, the following compounds represented by the following general formula (I) are used:



wherein

X^- represents an anion and

A^+ represents an onium ion selected from the group consisting of a iodonium, a substituted ammonium ion (except for NH_4^+) and a phosphonium ion, wherein as an onium compound a phosphonium compound is the most preferred.

The said phosphonium compound is generally represented by the general formula (II)



wherein :

each of R_1 and R_3 (same or different) represents hydrogen, an alkyl group, a substituted alkyl group, a cycloalkyl group, an aryl group or a substituted aryl group,
 R_2 represents any of the said groups represented by R_1 and R_3 or the atoms necessary to close a heterocyclic nucleus with either R_1 or R_3 ,
 the said onium ion being linked

- 1) to a polymer chain, or
- 2) via a bivalent organic linking group e.g., -O-, -S-, SO_2 -, ... to any other of such onium structure, or
- 3) directly to any of the groups represented by R_1 .

Suitable examples of the said phosphonium compounds are disclosed in US-A 3,017,270. In said specification suitable examples are mentioned of cationic polyalkylene oxide salts including e.g. quaternary ammonium and phosphonium and bis-quaternary salts.

Onium salt polymers wherein the onium group may be e.g. a phosphonium group, are disclosed in US-A 4,525,446. Other onium compounds as e.g. sulphonium compounds as disclosed in e.g. in EP-Specification 0 392 092 may also be used in minor amounts in combination with the preferred phosphonium compounds, used in the method of preparing emulsions according to this invention.

A preferred co-stabilising phosphonium compound used in the method according to the present invention is $(\text{Phen})_3\text{-P}^+\text{-CH}_2\text{-CH}_2\text{OH.Cl}^-$, wherein Phen represents phenyl as has been described e.g. in EP-A 0 677 773. Especially this feature is illustrative for

the protective action of the silica sol in the presence of an onium compound, thereby acting as a "network-stabilising" agent. The said phosphonium compound therein is moreover controlling and (co-)stabilising the preferred crystal habit of the regular (cubic or octahedral) or tabular ($\{111\}$ or $\{100\}$) silver halide crystals during nucleation and crystal growth in the silver halide precipitation step of the method according to this invention. As a composition of the said silver halide crystals any combination of chloride, bromide and iodide is possible.

In the precipitation conditions mentioned hereinbefore it is possible, not only to get very homogenous silver halide crystal size distributions, but also perfectly predictable average crystal sizes in order to guarantee a perfect scaling up.

According to the present invention silver halide emulsion crystals are chemically ripened in the presence of an onium precursor compound together with a combination of compounds generating sensitisation specks comprising silver, gold and selenium or silver, gold, selenium and sulphur. As silver is already present at the surface of the silver halide emulsion crystals, a combination of the said compounds generating gold and sulphur, if present, together with at least one selenium compound present in the form of a phosphonium precursor compound is used, said precursor compound having a structure corresponding to the general formula (III):



wherein R^1 , R^2 and R^3 have the same meaning as given hereinbefore.

According to the method of this invention the preferred onium compound and the said onium precursor compound are both phosphonium compounds.

The light-sensitive silver halide emulsion prepared in accordance with the method of the present invention is thus present as a so-called primitive emulsion as long as no sulphur, selenium or gold compounds or selenium and gold are added to the reaction vessel. According to the method of the present invention chemical sensitisation proceeds with a combination of gold and selenium or gold, selenium and sulphur.

Sulphur and gold compounds used as chemical sensitizers have been 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). In this literature chemical sensitisation can be carried out by effecting the chemical ripening in the presence of small amounts of compounds containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodanines. Selenium compounds which, apart from onium precursor compounds, are generating selenium as disclosed hereinbefore, can be used during chemical ripening and have e.g. been described in US-P 5,112,733 wherein chemical sensitisation is further performed in the presence of a palladium compound. In EP-A 0 443 453 thick tabular grain emulsions having an average aspect ratio from 3 to 8 and ten or more dislocation lines per grain are e.g. chemically sensitised with at least one selenium sensitiser, at least one gold sensitiser and at least one sulphur sensitiser. Further in EP-Specification 0 506 009 an analogous formula as formula (III) has been set forth wherein R^1 represents a substituted phenyl or a condensed aryl group, an alifatic group or a heterocyclic group; wherein R^2 and R^3 represent an alifatic, an aromatic or a heterocyclic group; and wherein (R^1) , (R^2) or (R^3) may be combined to form a ring together with the phosphorus atom. Substitution of phenyl groups with e.g. carboxylic acid or sulphonic acid groups is in favour of solubility in aqueous solutions and/or of lability characteristics, thereby influencing chemical ripening kinetics. Other references wherein selenium compounds are favourably used in the chemical ripening step are e.g. US-A's 4,565,778; 4,808,516; 4,810,626; 5,166,045; 5,114,838; 5,242,791; 5,397,692; 5,468,602; EP-A's 0 122 125; 0 300 382; 0 563 708; 0 638 840 and 0 712 034 and JP-A's 01187544 and 04295842.

In another embodiment tellurium compounds may partially replace selenium compounds.

Preferred amounts of said sulphur, selenium and gold compounds added during the chemical ripening step are depending on the crystal size (crystal surface available) of the emulsion crystals, but, according to this invention in order to get a preferred fog-sensitivity relationship, the formation of sensitisation specks comprising silver, gold and selenium or silver, gold, selenium and sulphur during the step of chemically ripening the said silver halide requires

- addition of compounds generating selenium in a molar ratio versus gold from 1:10 to 10:1;
- addition of compounds generating sulphur in an amount being not less than in optimised sulphur and gold chemically ripening compositions in the absence of selenium; and further
- addition of compounds generating sulphur versus compounds generating selenium in a molar ratio of from 1:5 to 5:1 and
- addition of the sum of compounds generating sulphur and selenium versus compounds generating gold in a molar ratio of from 3:1 to less than 15:1.

The said molar ratios are illustrative for the fact that higher amounts of selenium are needed, unless higher amounts of gold are present in order to suppress fog as will be illustrated in the Examples hereinafter.

The emulsions sensitised by means of gold-sulphur-selenium or gold-selenium ripeners as in the present invention can be treated before chemical sensitisation with reductors as e.g. tin compounds as has been described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphonic acids, and silane compounds. Chemical sensitisation can also be performed in the presence of small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitisation methods or a combination thereof can be used. A mixture can also be made of two or more separately precipitated emulsions being chemically sensitised before mixing them.

According to the method of this invention desalting of the reaction medium proceeds before, during and/or after chemically ripening the said silver halide, whereas redispersing of the silver halide proceeds before, during or after chemically ripening the said silver halide. Said desalting may proceed by flocculation as has been described e.g. in EP-A's 0 517 961 and 0 704 749 or by ultrafiltration.

According to the method of this invention the step of spectrally sensitising the silver halide crystals is further included, wherein chemical ripening is performed before, during and/or after the said step. It has been found that in a preferred embodiment chemical sensitisation is performed after addition of the spectral sensitiser(s), which can be added integrally, in portions or consecutive. Said addition of spectral sensitiser may be performed already during the precipitation step.

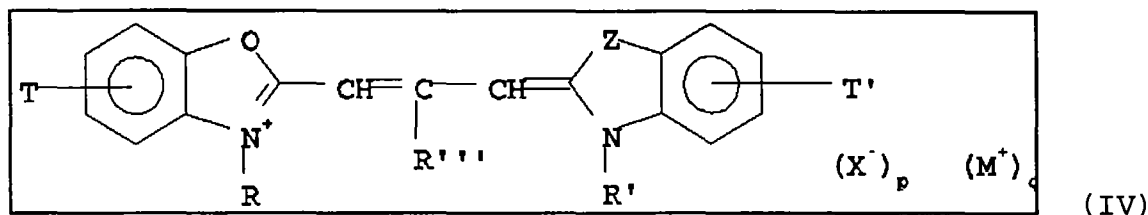
If onium precursor compounds according to the formula (III) are added during precipitation of silver halide regular or tabular grains the onium precursor compound, depending on its structure, decomposes as a function of time after being added to the reaction vessel and generates selenium which acts as a ripening agent during precipitation of silver halide crystals, further reacting to form a chemical sensitisation speck together with silver and gold or silver, gold and sulphur.

Depending on the precipitation medium and precipitation rate phosphonium ions generated from the same onium precursor compound are moreover acting as extra network stabilising agents, thereby colloiddally stabilising the said crystals. Addition of gold compounds during precipitation is also possible: there is moreover, as colloidal silica is used as a sole protective colloid during precipitation, no disadvantage as observed after precipitation in gelatinous medium wherein part of the gold compounds forms complexes with the gelatinous binder, thereby reducing its ripening activity and causing instability during preservation. As sensitisation specks composed of silver, gold and selenium or silver, gold, selenium and sulphur are generated at whatever a moment during and/or after precipitation of silver halide, it is possible to controll the internal and surface sensitivity of the silver halide crystals prepared according to the method of this invention. Any combination of silver with gold and/or sulphur and/or selenium as chemical sensitisation speck can be generated in the method of this invention and compositions of the said specks will depend on amounts of chemical compounds added, on chemical ripening time, on chemical ripening temperature in the reaction medium wherein said chemical ripening proceeds and on conditions of pAg, determining the amount of silver ions present in the reaction medium.

Spectral sensitisation of the light-sensitive silver halide crystals can be performed 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 sensitisation include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, homopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, complex merocyanine dyes.

Other dyes, which per se do not have any spectral sensitisation activity, or certain other compounds, which do not substantially absorb visible radiation, can have a supersensitisation effect when they are incorporated together with said spectral sensitising agents into the emulsion. Suitable supersensitisers are i.a. heterocyclic mercapto compounds containing at least one electronegative substituent as described e.g. in US-A 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described e.g. in US-A 2,933,390 and US-A 3,635,721, aromatic organic acid/formaldehyde condensation products as described e.g. in US-A 3,743,510, cadmium salts, and azaindene compounds.

In a preferred embodiment the preferred cubic and tabular silver halide emulsion crystals according to this invention are spectrally sensitised with at least one dye having a structure corresponding to the general formula (IV) given below,



wherein

Z represents a nitrogen or an oxygen atom and is substituted with R' if Z is a nitrogen atom,

R, R' and R'' each independently represent substituted or unsubstituted alkyl,

R''' represents hydrogen, substituted or unsubstituted alkyl or substituted or unsubstituted aryl,

T and T' each independently represent the usual substituents known in the art,

(X⁻)_p represents a negatively charged atom or group of atoms to compensate for the positive charge(s) present on the dye, and

(M⁺)_q represents a positively charged atom or group of atoms to compensate for the negative charge(s) present on the dye and wherein

p and q each represent an integer in order to get an electronically neutral compound.

Preferred spectral sensitizers suitable for use together with the emulsion crystals used in the method according to this invention are those of the type where

R''' is -C₂H₅, Z is an oxygen atom, and where at least one of R and R' represents

- a sulfoalkyl group, preferably corresponding to the formulae

- (CH₂)_nSO₃⁻ wherein n equals 2, 3 or 4,

- (CH₂)₂-CH(CH₃)-SO₃⁻

and

- CH₂-CHY-CH₂-SO₃⁻ wherein Y represents -OH or -Cl;

- a sulphatoalkyl group, preferably corresponding to the formula

- (CH₂)_nOSO₃⁻ wherein n equals 2, 3 or 4,

- an acylsulphonamido group, preferably corresponding to the formulae

- (CH₂)_n-C(O)-N(R''''')-SO₂-(CH₂)_mH wherein n equals 1, 2 or 3; m equals 1, 2, 3, etc.

- (CH₂)_r-SO₂-N(R''''')-SO₂-(CH₂)_sH wherein r equals 2, 3 or 4; s equals 1, 2, 3, etc.,

- (CH₂)_v-SO₂-N(R''''')-C(O)-(CH₂)_wH wherein v equals 2, 3 or 4; w equals 1, 2, 3, etc.

wherein R'''' represents H or alkyl; and wherein T and T' each independently represent 5-phenyl, 5-Cl, 5-OCH₃ or 5-CH₃.

Another class of preferred spectral sensitizers suitable for use together with the emulsion crystals according to this invention are those of the type where R''' is hydrogen, Z is a nitrogen atom;

wherein T represents 5-phenyl, 5-Cl, 5-OCH₃ or 5-CH₃ and wherein T' represents 5,6-(Cl)₂; 5-CN-6-Cl; 5-CF₃-6-Cl; 5-Cl; 5-CN, 5-CF₃, 5-CHF₂, 5-SO₂CH₃, 5-SO₂R'''''' (R'''''' representing a fluoro-substituted or non-fluoro-substituted alkyl-group), 5-COOR'''''' and 5-SO₂-N(R^x)(R^y) or 5-CO-N(R^x)(R^y), wherein R^x and R^y may each independently represent

substituted or unsubstituted alkyl groups, or which may each independently or together form a ring with the N-atom to which they are attached.

Especially preferred structures of the type wherein Z represents oxygen are those wherein T and T' each represent Cl or T represents Cl and T' represents Phenyl or vice versa and wherein R and R' each independently represent one of the combinations of the formulae

- (CH₂)_nSO₃⁻ wherein n equals 2, 3 or 4,

- (CH₂)₂-CH(CH₃)-SO₃⁻

and

- CH₂-CHY-CH₂-SO₃⁻ wherein Y represents -OH or -Cl;

and wherein R, represents one of the formulae given above and R' corresponds to one of the formulae

- (CH₂)_pH wherein p equals 1, 2, 3 or 4;

- CH₂-Phen-SO₃⁻

- CH₂-Phen-COOH

- (CH₂)_q-Phen-COOH wherein q equals 1, 2 or 3.

An example of an especially preferred spectral sensitizer according to the general formula (IV) given above is anhy-

dro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyloxacarbocyanine hydroxide or anhydro-5,5'-dichloro-3,3'-bis(n-sulphopropyl)-9-ethyloxacarbocyanine hydroxide. It has been established that silver halide emulsion crystals prepared in silica, spectrally sensitised with the preferred oxacarbocyanines show higher absorption signals in the spectra of their J-aggregates than corresponding silver halide crystals prepared in gelatin for the same surface coverage. This may consequently lead to an increased speed for silica emulsions. A control solution with colloidal silica particles in the absence of silver halide crystals and in the presence of the same spectral sensitiser doesn't show the presence of J-aggregates.

In a preferred embodiment according to this invention a benzimidazolocarbo-cyanine spectral sensitiser is used together with a sensitiser according to the formula (IV).

A suitable mixture of spectral sensitisers that is advantageously applied is anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyl oxacarbocyanine or anhydro-5,5'-dichloro-3,3'-bis(n-sulphopropyl)-9-ethyloxacarbocyanine together with anhydro-5,5'-dicyano-1,1'-diethyl-3,3'-di(2-acetoxyethyl)ethyl-imidacarbocyanine provided with suitable charge correcting ions for the respective compounds.

Embedded in a photographic material the regular or tabular silver halide crystals prepared according to the method of this invention are surrounded by colloidal silica, serving as an extremely useful protective colloid. An advantageous effect resulting therefrom is the better resistance of the coated material to pressure phenomena. Emulsion layers coated with emulsions having crystals prepared in accordance with the method of the present invention, and more particularly thin emulsion layers, are showing remarkable improvements concerning both resistance to stress and rapid processability if compared with conventional emulsions prepared in gelatinous medium. As the ratio by weight of gelatin to silver halide decreases more pronounced pressure marks can be expected. Nevertheless as a result of the protective action of the "network-stabilised" silica adsorbed to the silver halide crystal surface, much less pressure sensitivity appears. In addition thereto a clearly improved fog level besides a decreased pressure sensitivity for the coated emulsions in various processing conditions can be attained.

Silver halide photographic materials comprising light-sensitive emulsion layers comprising crystals prepared according to the method according to this invention are further fundamentally different from materials described e.g. in JP-A 04 340 951, wherein colloidal silica is used: although being advantageous with respect to pressure sensitivity, the colloidal silica used therein is not present as a protective colloid in the preparation of silver halide crystals but as a simple additive in light-sensitive layers comprising silver halide grains with a selenium compound. Light-sensitive silver halide photographic materials according to the present invention however do comprise at least one hydrophilic light-sensitive silver halide emulsion layer from an emulsion prepared according to the method as set forth in the description hereinbefore.

It is of crucial importance that said materials comprise an amount of hydrogen-bridge forming polymer and silver halide in a weight ratio of from 0 to 0.40 and silica to silver halide in a weight ratio of from 0.01 to 0.30, and more preferably, as has been set forth in the application concurrently filed herewith, from 0.01 to 0.10, said amount of silver halide being expressed as an equivalent amount of silver nitrate.

The photographic silver halide emulsions prepared according to the method of this invention can be used in various types of photographic elements such as i.a. in photographic elements for so-called amateur and professional photography, for graphic arts, diffusion transfer reversal photographic elements, low-speed and high-speed photographic elements, X-ray materials, micrographic materials, photothermographic elements, direct-positive elements, etc..

In a preferred embodiment the photographic silver halide emulsions are used in X-ray materials: single-side coated as well as (symmetrically or asymmetrically) duplitzed materials, used in a system in combination with (identical or differing) intensifying phosphor screens. As single-side coated materials they can be used as laser films which are nowadays desired hardcopy materials for use in diagnostic imaging.

The following examples illustrate the invention without however being limited thereto.

EXAMPLES

Example 1

Emulsion A

In this Example tabular silver bromiodide grains having {111} main tabular crystal faces were prepared in silica as a protective colloid.

The following solutions were prepared :

- 2.52 l of a dispersion medium (C) containing 0.13 moles of potassium bromide and 56 ml of 15 % silica sol 'Kiesel-sol 500' (trademarked product of Bayer AG), was established at a temperature of 70 °C and pH was adjusted to 3.0;
- a solution (N) containing 18 ml of a 5 % solution of co-stabilising phosphonium compound (Phen)₃-P⁺-CH₂-

CH₂OH.Cl⁻, wherein Phen represents phenyl. The pH value was adjusted to a value of 3.0.

- 500 ml of a 2.94 molar solution of silver nitrate (A);
- a solution containing 1.47 moles of potassium bromide (B1)
- a solution containing 1.45 moles of potassium bromide and 0.02 mole of potassium iodide (B2).

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Before the start of the precipitation solution N was added to solution C. Solution C was then stirred for 5 minutes.

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 19 min 111 ml of 15 % silica sol 'Kieselso 500' (trademarked product of Bayer AG) and 37 ml of a 5 % solution of co-stabilising phosphonium compound (Phen)₃-P⁺-CH₂-CH₂OH.Cl⁻, wherein Phen represents phenyl were added to solution C with 302 ml of demineralised water. The pH value was readjusted to a value of 3.0 and the solution was stirred for another 5 minutes.

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Then a growth step was performed by introducing by a double jet during 158 seconds solution A at a flow rate of 2.5 ml/min and solution B1 at a flow rate as to maintain a constant mV-value, measured by a silver electrode versus a Ag/AgCl Ingold reference electrode, of +10 mV (pAg=8.71). After this stage the flow rate of solution A was increased linearly over a period of 29 minutes to 7 ml/min, while the flow rate of solution B1 was increasing in order to maintain the said constant mV-value.

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Another physical ripening step of 5 minutes was performed. A second growth step was performed by introducing by a double jet during 354 seconds solution A at a flow rate of 2.5 ml/min and solution B2 at a flow rate in order to maintain the said constant mV-value, measured by a silver electrode versus a Ag/AgCl Ingold reference electrode, of +10 mV (pAg=8.71). After this stage the flow rate of solution A was increased linearly over a period of 41 minutes and 22 seconds to 12.5 ml/min, while the flow rate of solution B2 was increased in order to maintain the constant mV-value.

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After the said precipitation 25 g of inert gelatine was added to the emulsion and the emulsion was stirred for another 5 minutes. The emulsion was then desalted.

The thus obtained emulsion comprising silver bromoiodide tabular grains having 1 mole % of iodide ions based on silver, comprised a high percentage by number (at least 90 %) of tabular grains, having an aspect ratio of more than 5 which was counted from the corresponding electron microscopic photographs, having a mean ECD (equivalent circular diameter) of 1,14 μm and a mean thickness of 0.130 μm.

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During the redispersion of the emulsions an amount of inert gelatin was added in order to obtain a ratio by weight of gelatin to silver halide (expressed as silver nitrate) of 0.3, the emulsion containing an amount of silver bromoiodide equivalent with 175 g of silver nitrate per kg.

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The emulsion was divided in several portions (1 - 5) and chemically ripened as follows.

Chemical sensitisation 1 (comparative):

Portion 1 of emulsion A was set at 50°C and the UAg value was adjusted to + 80 mV (pAg = 8.21), measured by making use of a silver electrode versus a Ag/AgCl Ingold reference electrode and as a spectral sensitiser, anhydro- 5,5'-dichloro-3,3'-bis-(n.sulfobutyl)-9-ethyloxacarbo-cyanine triethylamine was added in an amount of 0.09 x 10⁻³ mole per mole of silver nitrate. The emulsion was ripened with sulphur and gold ions. Amounts of ripening agents were adapted to the crystal size of the emulsion crystals.

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Chemical ripening agents were gold thiocyanate, sodium thiosulphate and toluene thiosulphonic acid, which was used as predigestion agent. The said amounts of each chemical ripening agent were optimised in order to obtain an optimal fog-sensitivity relationship after 4 hours at 50°C.

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Chemical sensitisation 2 and 3 (invention); 4 and 5:

Portions 2 to 5 of emulsion A were set at 50°C and the UAg was adjusted to + 80 mV (pAg = 8.21), measured by means of a silver electrode versus a Ag/AgCl Ingold reference electrode and as a spectral sensitiser, anhydro- 5,5'-dichloro-3,3'-bis-(n.sulfobutyl)-9-ethyloxacarbo-cyanine triethylamine was added in an amount of 0.89 x 10⁻³ mole per mole of silver nitrate. The emulsions were ripened with sulphur, gold and selenium. Amounts of ripening agents were adapted to the crystal size of the emulsion. Chemical ripening agents were gold thiocyanate, sodium thiosulphate, triphenylphosphorselenide and toluene thiosulphonic acid which was used as predigestion agent. Amounts of each chemical ripening agent were varied as set forth in Table 1, and the time of ripening was adjusted in order to obtain an optimal fog-sensitivity relationship.

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Before coating the chemically sensitised emulsions 1 to 5 were stabilised with 1-p-carboxy-phenyl-5-mercapto-tetrazole. The emulsions were coated in a hydrophilic coating layer on a polyester support and were illuminated in the wet state. After drying the sensitivity was measured with a densitometer.

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The results obtained for the said emulsion samples Nos. 1-5 are summarised in Table 1, wherein amounts of addenda are expressed in μmole per mole of silver nitrate. Values of fog densities are multiplied by a factor of 100. The

same applies to sensitivity values which are expressed as relative log It numbers: a decrease with a value of 30 is indicative for an enhancement in speed with a factor of 2.

Table 1

Sample	Sulphur	Gold	Selenium	Fog	Sensit.	Dmax
1(comp.)	15.1	1.7	-	2	234	372
2(inv.)	18.9	4.4	37.9	3	141	388
3(inv.)	30.1	6.9	15.1	1	148	391
4	7.5	1.7	15.1	2	253	273
5	15.1	1.7	15.1	*	**	380

*: intolerably high; **: not measurable

As can be seen from Table 1 addition of selenium (as in sample No. 5) to optimised amounts of sulphur and gold (see comparative sample No. 1) is inadmissible. Moreover it is not obvious to replace sulphur partially by a selenium compound (sample No. 1 vs. No. 4).

On the other hand it can be concluded that the use of selenium in combination with sulphur and gold remarkably improves speed and offers an optimised fog-sensitivity relationship when the selenium compound is added in molar amounts versus sulphur and gold respectively, and in amounts together with sulphur versus gold as set forth in the detailed description. As can be expected the generated co-stabilising phosphonium compound resulting from the breaking of the labile P-Se bond interferes with the $(\text{Phen})_3\text{-P}^+\text{-CH}_2\text{-CH}_2\text{OH.Cl}^-$ co-stabiliser and further contributes the stabilisation of the emulsion.

It can also be concluded that the presence of higher amounts of gold permits the use of higher amounts of sulphur, but lower amounts of selenium in the chemical ripening process (see invention sample No. 3).

Example 2

Emulsion B

In this Example silver bromiodide grains having a cubic habit were prepared in silica sol as a protective colloid.

A photographic silver iodobromide emulsion containing 1.0 mole % of silver iodide was prepared by the double jet method in a vessel containing 642 ml of demineralised water, 300 ml of 15 % silica sol 'Kieselso 500' (trademarked product of Bayer AG), 225 mg of 3,6-dithio-1,8-octanediol as a grain growth accelerator, and 72 ml of a 5 % solution of co-stabilising phosphonium compound $(\text{Phen})_3\text{-P}^+\text{-CH}_2\text{-CH}_2\text{OH.Cl}^-$, wherein Phen represents phenyl. The temperature was stabilised at 50°C and the pH value was adjusted to a value of 3.0.

During 5 minutes, a silver nitrate solution (2.94 M) was added to the reaction vessel at a constant flow rate of 8 ml/min. Simultaneously a mixed halide solution (99 mole % of KBr and 1 mole % of KI), having the same molarity of the AgNO_3 solution was added to the said vessel at a flow rate of the mixed halide salt solution in order to adjust the pAg value at +138 mV ($\text{pAg} = 7.30$) vs. a silver electrode versus a Ag/AgCl Ingold reference electrode, throughout this precipitation stage. Mixing of both salt solutions was performed with central stirring means at 500 rpm. After the said 5 minutes the flow rate of the silver nitrate solution was increased continuously up to 16 ml/min during 80 minutes. The mixed halide solution was further added at an addition rate in order to maintain the same constant pAg value.

The emulsions obtained comprised crystals having a {100} cubic habit and had an average grain size based on volume of around 0.60 μm . The homogeneity of the silver halide grain distribution expressed as the variation on the mean grain size is equal to around 20 %. The obtained cubic AgBr(I) emulsion precipitated in silica was then divided in 3 separate portions.

During the redispersion of the emulsion inert gelatin was added in order to obtain a ratio by weight of gelatin to silver halide (expressed as silver nitrate) of 0.24, the emulsion containing an amount of silver bromiodide equivalent with 188 g of silver nitrate per kg.

Chemical sensitisation 1 (comparative)

Portion 1 of emulsion B was chemically ripened in the classical way with sulphur and gold, at a UAg value adjusted at + 78 mV ($\text{pAg} = 8.36$), measured by means of a silver electrode versus a Ag/AgCl Ingold reference electrode, at 46°C

for 3 hours in order to get an optimised relationship between fog and sensitivity. Chemical ripening agents were gold thiocyanate, sodium thiosulphate and toluene thiosulphonic acid which was used as a predigestion agent. After ripening as spectral sensitiser, anhydro- 5,5'-dichloro-3,3'-bis(n.sulfobutyl)-9-ethyloxacarbo-cyanine hydroxide and anhydro-5,5'-dicyano- 1,1'-diethyl-3,3'-di(2-acetoxyethyl)ethyl-imidacarbocyanine bromide were added in amounts of 0.40 mmole and 0.24 mmole per mole of silver nitrate respectively.

Chemical sensitisation 2 and 3 (inventive)

Chemical ripening agents for sample No. 2 and sample No. 3 (invention) were gold thiocyanate, sodium thiosulphate, triphenylphosphorselenide and toluene thiosulphonic acid which was again used as predigestion agent. Amounts of each chemical ripening agent were varied as set forth in Table 1, and the time of ripening was adjusted in order to obtain an optimal fog-sensitivity relationship. Spectral sensitisation was performed in the same way as for sample No. 1 hereinbefore.

The chemically sensitised emulsions (samples Nos. 1 to 3) were coated in a hydrophilic coating layer on a polyester support and were illuminated in the wet state. After drying the sensitivity was measured with a densitometer.

The results obtained for the said emulsion samples Nos. 1 to 3 are summarised in Table 2, wherein amounts of addenda are expressed in μ mole per mole of silver nitrate. Values of fog densities and relative sensitivity values are expressed as relative log It numbers, just as in Table 1.

Table 2

Sample	Sulphur	Gold	Selenium	Fog	Sensit.	Dmax
1(comp.)	21.4	35	-	4	182	283
2	21.4	35	129	31	157	264
3(inv.)	42.8	17	64.6	5	163	272

As can be seen from Table 2 by introducing an additional amount of selenium during ripening of the cubic silver bromide crystals the sensitivity is remarkably improved (sample No. 1 vs No. 2). However fog had a tremendously increased value too, so that further investigation of the chemical ripening was required.

An overall improved sensitometry was obtained for the silver bromide emulsion crystals precipitated in colloidal silica sol as a protective colloid by making use of a combination of sulphur, selenium and gold as for sample No. 3 (invention) according to the conditions set forth in the detailed description. Obviously ripening of cubic crystals requires higher amounts of gold and a lower molar ratio of the sum of sulphur and selenium compounds versus gold (lower than 10:1).

Claims

1. Method of preparing a light-sensitive silver halide emulsion comprising the steps of:

- precipitating silver halide by means of a double-jet or a triple-jet technique in a reaction medium comprising colloidal silica as a protective colloid in the absence of any polymeric compound capable of forming hydrogen bridges with colloidal silica but in the presence of one or more onium compounds, said colloidal silica having an average particle diameter from 0.003 μ m to 0.30 μ m, the ratio by weight of onium compound(s) to silica being between 0.03 and 0.3 at every moment during precipitation and the ratio by weight of silica to silver halide, expressed as an equivalent amount of silver nitrate, being from 0.01 to 0.3 at the end of precipitation;
- desalting the reaction medium;
- redispersing the silver halide; and
- chemically ripening the said silver halide in the presence of an onium precursor compound together with a combination of compounds in order to generate sensitisation specks comprising silver, gold and selenium or silver, gold, selenium and sulphur.

2. Method according to claim 1, wherein the ratio by weight of silica to silver halide, expressed as an equivalent amount of silver nitrate, is from 0.01 to 0.1 at the end of precipitation.

3. Method according to claim 1 or 2, wherein the step of desalting the reaction medium proceeds before, during and/or after chemically ripening the said silver halide.

4. Method according to claim 1 or 2, wherein the step of redispersing the silver halide proceeds before, during or after chemically ripening the said silver halide.
5. Method according to any of claims 1 to 4, further including the step of spectrally sensitising the silver halide before, during and/or after the said step of chemically ripening the silver halide.
6. Method according to any of claims 1 to 5, wherein the said onium compound and the said onium precursor compound are both phosphonium compounds.
7. Method according to any of claims 1 to 5, wherein the said onium compound is $(\text{Phen})_3\text{-P}^+\text{-CH}_2\text{-CH}_2\text{OH.Cl}^-$ wherein Phen represents phenyl.
8. Method according to any of claims 1 to 5, wherein the said onium precursor compound is a compound represented by the formula $(\text{Phen})_3\text{-P=Se}$, wherein Phen represents phenyl.
9. Method according to any of claims 1 to 8, wherein sensitisation specks comprising silver, gold and selenium or silver, gold, selenium and sulphur formed during the step of chemically ripening the said silver halide require
- addition of compounds generating selenium in a molar ratio versus gold from 1:10 to 10:1;
 - addition of compounds generating sulphur in an amount being not less than in optimised sulphur and gold chemically ripening compositions in the absence of selenium;
 - addition of sulphur versus selenium in a molar ratio of from 1:5 to 5:1 and
 - addition of the sum of compounds generating sulphur and selenium versus compounds generating gold in a molar ratio of from 3:1 to less than 15:1.
10. Method according to any of claims 1 to 9, wherein said silver halide has a regular or a tabular crystal habit.
11. Light-sensitive silver halide photographic material comprising at least one hydrophilic light-sensitive silver halide emulsion layer from an emulsion prepared according to the method of any of claims 1 to 10.
12. Light-sensitive silver halide photographic material according to claim 11, wherein said emulsion layer comprises an amount of hydrogen-bridge forming polymer and silver halide in a weight ratio of from 0 to 0.40 and an amount of silica and silver halide in a weight ratio of from 0.01 to 0.30, said amount of silver halide being expressed as an equivalent amount of silver nitrate.
13. Light-sensitive silver halide photographic material according to claim 12, wherein said weight ratio of silica to silver-halide is from 0.01 to 0.10.



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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 2612

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	EP 0 677 773 A (AGFA GEVAERT NV) 18 October 1995 * page 8, line 17 - line 29; claim 7 * ---	1,11	G03C1/09 G03C1/04
D,A	DATABASE WPI Section PQ, Week 9302 Derwent Publications Ltd., London, GB; Class P83, AN 93-013262 XP002027557 & JP 04 340 951 A (FUJI PHOTO FILM CO LTD) , 27 November 1992 * abstract * ---	1,11	
A	DATABASE WPI Section PQ, Week 9401 Derwent Publications Ltd., London, GB; Class P83, AN 94-002672 XP002027558 & JP 05 313 293 A (FUJI PHOTO FILM CO LTD) , 26 November 1993 * abstract * ---	1,11	
A	EP 0 443 453 A (FUJI PHOTO FILM CO LTD) 28 August 1991 * page 7, line 35 - page 9, line 11; claim 1 * * page 14, line 24 * ---	1,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) G03C
A	EP 0 428 041 A (FUJI PHOTO FILM CO LTD) 22 May 1991 * page 8, line 40 - page 9, line 9; claim 1; tables 5,8,10 * -----	1,11	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 March 1997	Examiner Bolger, W
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	

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