

June 18, 1974

F. H. CLAES ET AL

3,817,756

MANUFACTURE OF PHOTOGRAPHIC SILVER HALIDE MATERIALS

Filed May 9, 1972

4 Sheets-Sheet 1

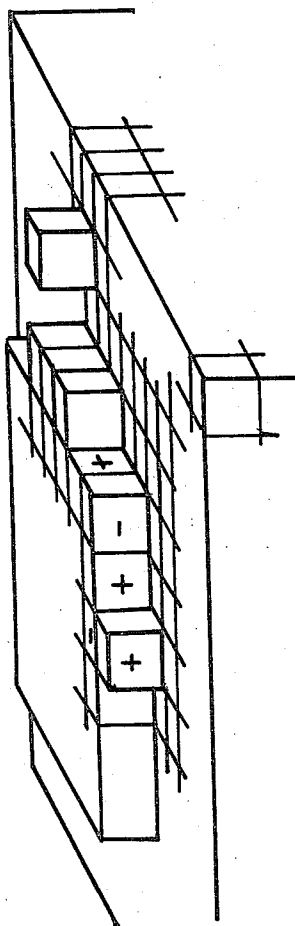


FIG. 2

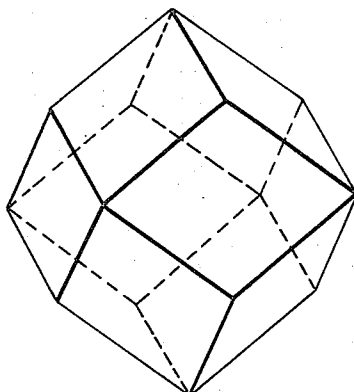


FIG. 1

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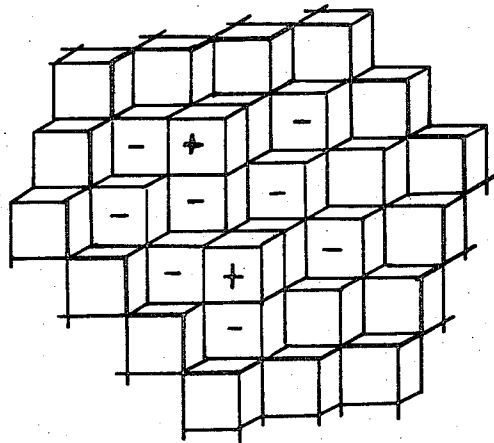


FIG. 4

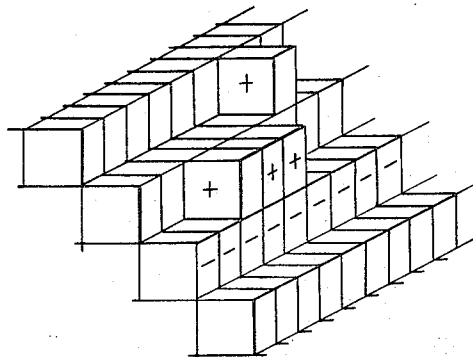


FIG. 3

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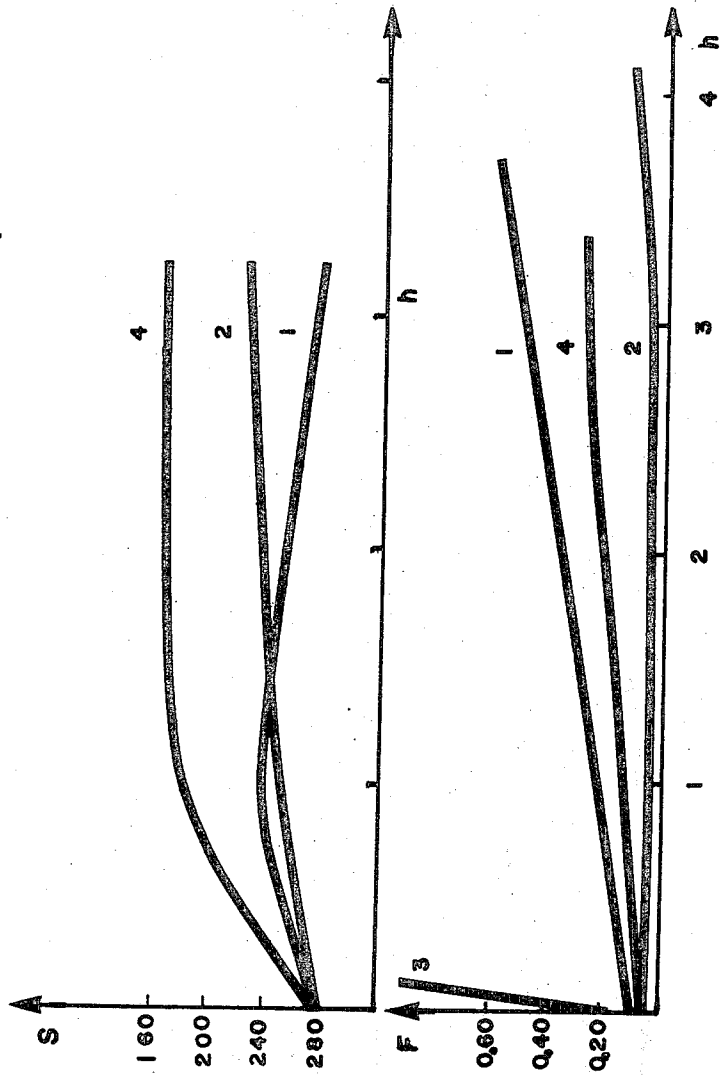


FIG. 5

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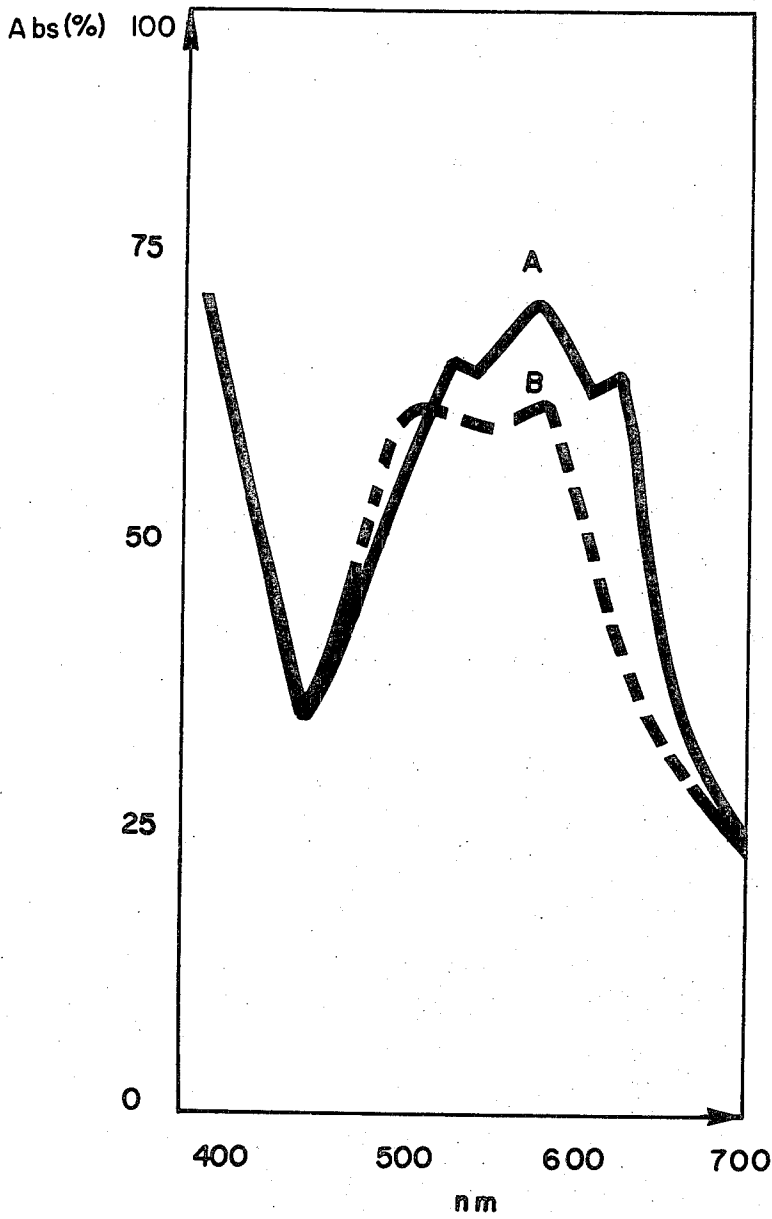


FIG. 6

1

2

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MANUFACTURE OF PHOTOGRAPHIC SILVER HALIDE MATERIALS

Frans Henri Claes and Marcel Jan Libeer, Mortsels, and Willy Joseph Vanassche, Aartselaar, Belgium, assignors to Agfa-Gevaert N.V., Mortsels, Belgium

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U.S. Cl. 96-94 R

12 Claims

ABSTRACT OF THE DISCLOSURE

A photographic material containing silver chloride and/or silver chlorobromide grains that have (110) crystal planes which grains are dispersed in a binder layer. The adsorption of sensitizing dyes on the {110} habit grains is different from that of {100} habit grains.

The present invention relates to a photographic silver halide material, its manufacture and use.

It is known to prepare photosensitive silver halide crystals by a precipitation technique starting from a water-soluble halide and a water-soluble silver salt in the presence of a protective colloid.

It is also known e.g. from Frieser, H. et al.—"Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden"—Akademische Verlagsgesellschaft—Frankfurt Am Main—Federal Republic of Germany (1968), pp. 631-640, that the environment in which the precipitation takes place has an influence on the crystal habit of the silver halide grains.

A survey of techniques that can be applied in the control of the crystal habit of silver bromide was described by F. H. Claes and W. Peelaers in PS&E, vol. 12, 1968, pp. 207-212. In this article the transition of regular or twinned cubic silver bromide crystals with {100} habit characterized by (100) planes, into octahedral crystals with {111} habit and having (111) planes is discussed in detail.

In silver halide photographic materials silver halide grains having the {100} and {111} crystal habit have been used thus far. No crystals with {110} habit have been described for photographic purposes.

Since the crystal habit of the light-sensitive silver halide plays a role in the physical and chemical processes that are characteristic for the manufacture and processing of photographic materials containing silver halide, research is directed to the production of light-sensitive silver halide microcrystals that have a particular crystal structure and as a result of such structure have special properties desired in the photographic materials and process.

According to the present invention photosensitive recording materials are provided, which contain, dispersed in a binder, silver chloride grains and/or silver chlorobromide grains that preferably contain at most 90 mole percent of bromide, which grains have (110) crystal planes.

According to a preferred embodiment said crystals are present in a recording layer containing a film-forming hydrophilic colloid as binder for said crystals.

The crystals when being regular (not twinned) and solely containing (110) planes have the shape of a regular rhombododecahedron.

In the accompanying drawings 1 to 4 different crystal structures of such silver halide are illustrated.

FIG. 1 represents a regular rhombododecahedron.

In the FIGS. 2, 3, and 4 silver halide crystal structures representing the arrangement of the atoms in (100), (110), and (111) planes respectively are illustrated.

These figures illustrate in subsequent order the different crystal lattice structures characteristic for cubic, rhombododecahedral and octahedral silver chloride crystals. The cubes representing the silver ions are marked with a plus sign (+) and the cubes representing the chloride ions are marked with a minus sign (-).

Details about silver halide crystals having a cubic or octahedron habit are given by G. F. Duffin, in Photographic Emulsion Chemistry—The Focal Press, London (1966), pp. 66-74.

Silver chloride and silver chlorobromide crystals suited for the purpose of the invention and in which (110) planes can be recognized are prepared by carrying out the silver halide crystal lattice formation (nucleation) or crystal growth under special conditions as described herein.

According to a preferred embodiment for preparing such grains the formation by precipitation and/or the grain growth of silver chloride crystals and/or silver chlorobromide crystals containing at most 90 mole percent of bromide is carried out in aqueous medium in the presence of a protective hydrophilic colloid and a substance or substances that when incorporated in an aqueous solution containing a dye partly in its aggregated and partly in monomeric (i.e. non-aggregated) form enhance(s) the intensity of the absorption band characteristic of the monomers of the dye.

A wide variety of said substances having this property of enhancing the intensity of the monomer absorption band is at one's disposal, and although not all the substances that give a positive result in the test as described hereinafter will be active in the formation of silver chloride or silver chlorobromide crystals with (110) planes, the great majority (more than 80%) will do so.

A definite chemical classification of said substance(s) has been found quite impossible.

In a test convenient for said selection the substance to be tested is dissolved in water in a preferred amount of 1 gram per litre and added to an equal volume of an aqueous solution of methylene blue. The methylene blue is dissolved preferably in an amount of 20 mg. per litre. The absorption spectrum of the obtained mixture is compared with that of a same aqueous solution of methylene blue, to which an equal volume of pure water was added.

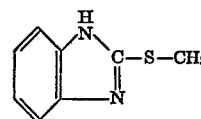
The association in aqueous solution of dye molecules was discussed by P. Mukerjee and A. K. Gosh, J. Phys. Chem., 67, 193 (1963) and the influence of particular organic substances such as 2-(4-pyridyl)benzimidazole on the spectrum of methylene blue was described by F. H. Claes and W. Peelaers in their article mentioned before.

The greater part of substances that enhance the monomer absorption band (the absorption band of the non-aggregated molecules) of the methylene blue is suited for use as substance controlling crystal habit and promoting the formation of silver chloride or silver chlorobromide containing (110) crystal planes.

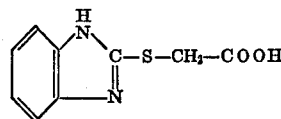
Substances that enhance the monomer absorption band characteristic under the above described test conditions are listed in the following Table.

TABLE

(1)

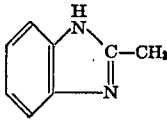


(2)

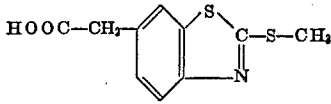


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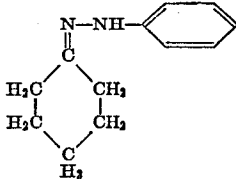
(3)



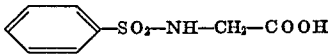
(4)



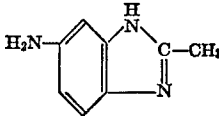
(5)



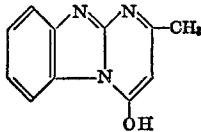
(6)



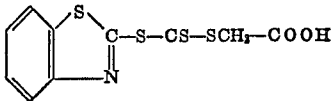
(7)



(8)



(9)



Some of these substances are known as fog-inhibiting or stabilizing agents (see for their preparation e.g. the United Kingdom Patent Specification 859,143). Others are known intermediate products in the preparation of spectral sensitizing agents.

In the manufacture of photographic recording materials according to the present invention the usual techniques known in silver halide emulsion preparation are used with the proviso, however, that somewhere in the stage of forming a crystal lattice containing silver chloride or the growing of crystals containing such lattice a substance providing (110) planes in the crystal structure is present in the medium in which the formation or growth of the crystals takes place.

Basically, the preparation of a silver halide emulsion comprises a number of stages, which are as follows:

(1) The formation of very small silver halide crystals starting from a precipitation reaction between a water-soluble halide and a water-soluble silver salt (emulsification).

(2) The growth of these crystals to the appropriate size (physical ripening).

(3) The removal of by-products resulting from the crystal formation and grain growth (washing).

(4) The sensitization of the crystals to obtain the desired response to light (chemical and spectral sensitization).

(5) The incorporation of additional ingredients, e.g. stabilizing agents, wetting agents, fog-inhibiting agents, development-accelerating compounds, colour couplers, etc. to make the emulsion ready for coating.

Thus the substances controlling the crystal habit and used according to the present invention will be applied in stage 1 and/or 2, not excluding, however, the embodiment in which one type of silver halide is converted in another type of silver halide e.g. by replacing other, e.g. 75

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bromide ions in an already existing silver halide salt grain by chloride ions, which is a technique applied for preparing so-called converted type emulsions.

According to an embodiment of the invention the first stage, which is also called emulsification or precipitation is achieved by mixing a solution containing a water-soluble chloride optionally combined with a limited amount of water-soluble bromide, with a solution of water-soluble silver salt in the presence of a protective colloid e.g. gelatin and said substance controlling the crystal habit.

The chloride and bromide may be that of an alkaline metal such as sodium or potassium, or alternatively ammonium chloride or bromide. The quantities of halide and silver ions need not be equivalent.

Apart from more modern ways of making photographic emulsions by continuous precipitation processes of which particular examples are illustrated in the Belgian Patent Specification 765,029, there are two broad classes of methods applied to form a silver halide emulsion.

The first of these is known as the single jet method. According to this procedure an aqueous silver salt solution e.g. silver nitrate solution is run through a jet, at a carefully controlled rate, into a stirred solution containing the halide, in the present invention a dissolved chloride optionally combined with a certain amount of bromide, a protective colloid e.g. gelatin, and other ingredients one of which is the substance controlling the crystal habit.

According to the second method, called the double-jet process, a solution of a water-soluble silver salt and a solution of the halide, equivalent to that of the silver salt e.g. silver nitrate are added simultaneously by two separate jets to a stirred solution of a protective colloid e.g. gelatin and optionally also a chloride. A further quantity of protective colloid is incorporated optionally into the halide solution and sometimes in the solution containing silver ions. According to this method the substance controlling the crystal habit is used preferably in the medium containing the protective colloid.

However, said substance need not be present from the very beginning of the precipitation and the crystals may have reached a certain size and habit already before the habit control and (110) plane formation is started.

The growth of the silver halide grains formed by precipitation to the appropriate size normally proceeds by thermal treatment. This is called physical ripening to distinguish it from the chemical ripening. In the physical ripening an amount of crystals grows at the expense of other crystals. This process is continued until the crystals have attained the desired grain size and grain size distribution.

According to an embodiment of the present invention the physical ripening of a silver halide emulsion containing silver chloride grains or silver chlorobromide grains with at most 90 mole percent of bromide is carried out in the presence of said substance controlling the crystal habit. The crystal growth will only occur in the presence of suitable silver halide solvents, usual representatives of which are disclosed by G. F. Duffin in the already mentioned book on pp. 59-60.

Growth will take place by the dissolution of surface ions from one crystal as a result of the action of the ripening agent, followed by their migration to a neighbouring crystal, where reprecipitation will occur in a crystal lattice determined by the environment of these ions. The substance controlling the crystal habit of use according to the present invention controls the sequence of arrangement of the silver and chloride ions or mixture of chloride and bromide ions in the lattice pattern in such a way that (110) planes characterized by step-faces are formed as illustrated in FIG. 3.

The amount of substance controlling the crystal habit is preferably in the range of about 10 to about 50 millimole per mole of silver chloride to be formed.

The substance controlling the crystal habit may be removed from the emulsion by washing after the desired crystal habit has been obtained. The substance controlling the crystal habit does not need but may be present in the emulsion as finally coated.

In the preparation of photographic materials that are developed and processed by means of aqueous liquids, preferably hydrophilic colloids known in the art such as gelatin are used as binder for the silver halide grains.

Preferred photographic materials according to the present invention contain at least one silver halide emulsion layer comprising as the sole photosensitive silver halide silver chloride grains containing (110) crystal planes, wherein said grains are dispersed in a hydrophilic colloid binder. The present invention includes, however, also such photographic materials in which these grains are present together with silver halide grains of another crystal habit or halide type or of which the crystal grains only partially contain (110) planes, e.g. they contain mixtures of (110) with (100) and of (110) with (111) planes.

The invention includes any method of forming a photographic image or record, which comprises information-wise or record-wise exposing to visible light or to other active radiation a material, which is sensitive to such radiation and which comprises silver chloride or silver chlorobromide grains having (110) crystal planes, such grains being dispersed in a binder, the said material preferably comprising a radiation-sensitive layer composed of micro-crystals of silver chloride and/or silver chloro-bromide grains having such planes and dispersed in a protective colloid binder.

Photographic silver halide emulsion materials containing silver chloride and/or silver chlorobromide crystals characterized by (110) crystal planes possess a lower tendency to fog than silver chloride emulsions containing the already known silver chloride crystals containing (100) crystal planes.

This property makes it possible to chemically sensitize the (110) type silver halide to a higher extent than the (100) type silver chloride crystals without surpassing an acceptable fog level. A practical test proving this advantage is given in the Examples 2 and 3, the test results of which are illustrated in FIG. 5.

Another remarkable advantage of photographic silver halide emulsion materials containing the (110) type crystals lies in the possibility to obtain therewith by means of a spectral sensitizing agent an increased spectral absorption in the shorter wavelengths and a decreased absorption in the higher wavelengths as compared with photographic materials containing (100) type silver chloride crystals. This different spectral sensitizability is probably due to another aggregation pattern of the sensitizing dye molecules on the (110) planes. A practical test proving this property is given in Example 4 and the results are shown in FIG. 6.

The photographic emulsions containing (110) type silver chloride and/or silver bromochloride crystals can be used for all photographic purposes known from silver halide photography, in other words, there is no photographic silver halide material, in which they cannot be used. So, they can be used, e.g., in black-and-white materials as well as in color materials, in negative materials as well as in reversal or direct positive materials e.g. of the composite (core-shell) grain type.

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

EXAMPLE 1

A 3 molar aqueous solution of silver nitrate and a 3 molar aqueous solution of sodium chloride were added at 60° C. to a stirred solution of 36 g. of gelatin dissolved in 500 ml. of distilled water. The rate of addition of said solutions was such that the pAg expressed in millivolts remained constantly at +300 mv. and the pH was kept at 5.8.

The precipitation was continued until a crystal grain size of about 0.4 micron was reached.

To 600 g. of the thus obtained silver chloride dispersion having a silver chloride content equivalent with 85 g. of silver nitrate were added 1.5 g. of the substance No. 2 controlling the crystal habit, which substance had been dissolved in 250 ml. of water.

The silver chloride precipitation was continued at a pAg expressed in millivolt of +70 mv. and a pH of 5.8.

The finally obtained silver chloride dispersion contained silver chloride grains having a practically pure rhombodecahedral shape.

The dispersion was freed from its water-soluble by-products by noodling and washing, and after remelting emulsion portions thereof were treated as described in the Examples 2, 3, and 4.

EXAMPLE 2

A gelatin silver chloride emulsion (emulsion B) prepared as described in Example 1 and a gelatin silver chloride emulsion (emulsion A) prepared as described in Example 1 but in the absence of the substance controlling the crystal habit, so that the silver chloride grains characterized by (100) planes, were sulphur-sensitized by adding thereto pro rata of 60 g. of silver chloride 1 mg. and 1.5 mg. of bis-(dimethylthiocarbamoyl)sulphide respectively.

The sulphur sensitization was carried out for both emulsions at the same temperature (46° C.), the same pH (6.00) and the same pAg (7.5).

The silver chloride emulsion A characterized by the {100} crystal habit grains reached maximum speed (the speed (S) is expressed in relative log *I*t values) very quickly under heavy fog (F) (fog is expressed in optical density values). The speed and fog results versus time expressed in hours (h.) can be learned from curves 1 of FIG. 5.

The behaviour of the silver chloride emulsion B characterized by {110} crystal habit was quite different: the speed (S) rose more slowly and the fog (F) remained rather unchanged with enhancing treating time (h.) (see curves 2 of FIG. 5).

The results of the sulphur sensitization of these tests are summarized in the following Table A.

TABLE A

Sensitometric values	Emulsion	
	A	B
Speed before ripening (rel. log <i>I</i> t).....	2.78	2.69
Fog (optical density before ripening).....	0.10	0.06
Maximum speed (rel. log <i>I</i> t).....	2.38	2.28
Fog (optical density) at maximum speed.....	0.24	0.07

The test strips of the emulsions A and B were developed for seven minutes at 20° C. in a developing bath having the following composition:

Monomethyl-p-aminophenol hemisulphate	g--	2
Hydroquinone	g--	5
Anhydrous sodium sulphite	g--	100
Borax	g--	10
Boric acid	g--	5
Potassium bromide	g--	0.5
Potassium iodide	mg--	4
Ethylene diamine tetraacetic acid trisodium salt	g--	1.5

EXAMPLE 3

Example 2 was repeated with the difference, however, that the chemical sensitization was a sulphur- and gold sensitization that was carried out with respect to the emulsion A with 1 mg. of bis-(dimethylthio carbamoyl)sulphide and 3 ml. of a 0.06% by weight solution of gold(I) thiocyanate. The chemical sensitization of emulsion B was carried out with 1.5 mg. of bis-(dimethylthiocarbam-

oyl)sulphide and 5 ml. of a 0.06% by weight solution of gold(I) thiocyanate in water.

Immediately after the addition of the ripening solutions the emulsion A with {100} habit became completely fogged (see curve 3 of FIG. 5). Because of the extremely high fog the speed could not be determined. The emulsion B with {110} habit could be ripened to maximum speed with acceptable fog (see curves 4 of FIG. 5).

The development of the test strips was the same as in Example 2.

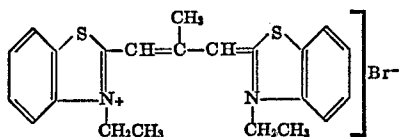
The results of the combined gold- and sulphur sensitization are summarized in the following Table B.

TABLE B

Sensitometric values	Emulsion	
	A	B
Speed before ripening (rel. log <i>I</i>)	2.76	2.69
Fog (optical density) immediately after addition of the ripening solutions	1.15	0.12
Speed after 1 hour	2.00	1.88
Fog after 1 hour	2.00	0.14

EXAMPLE 4

A gelatin silver chloride emulsion B prepared as described in Example 1 and a gelatin silver chloride emulsion A prepared as emulsion B but without substance controlling the habit were sensitized spectrally with a cyanine dye having the following structural formula:



The spectral sensitizing agent was added in an amount of 25 mg. per 50 g. of silver halide.

In the accompanying FIG. 6, the spectral absorption (expressed in percent with respect to the wavelength range of 400 to 700 nm.) of both emulsions A (curve A) and B (curve B) is given.

It appears that the emulsion B with {110} habit can be sensitized spectrally in a different way from that of emulsion A with {100} habit.

EXAMPLE 5

A gelatin silver chloride emulsion was prepared as described in Example 1 but in the absence of the substance controlling the crystal habit. The silver chloride grains obtained had a mean grain size of 0.4 micron.

To 600 g. of this emulsion 6 g. of the substance No. 2 controlling the crystal habit (see the table) and containing a carboxylic acid group dissolved in 30 ml. of water containing an amount of sodium hydroxide equivalent to the amount of said substance was added.

Subsequently the precipitation was continued with a 3 molar aqueous solution of silver nitrate and a 3 molar aqueous solution of a mixture of sodium chloride and potassium bromide (90:10 mole percent) at a pAg corresponding with an electromotive force (E.M.F.) of +90 mv. (Ag/saturated calomel electrode) and a pH of 5.8.

The thus obtained silver chlorobromide grains have a regular rhombododecahedral shape.

EXAMPLE 6

The procedure of Example 5 was repeated with the difference, however, that in the second precipitation stage a 3 molar aqueous solution of a mixture of sodium chloride and potassium bromide (50:50 mole percent) was used.

The obtained silver halide grains also had a regular rhombododecahedral shape.

EXAMPLE 7

The procedure of Example 5 was repeated with the difference, however, that in the second precipitation stage a 3 molar aqueous solution of sodium chloride and potassium bromide (25:75 mole percent) was used.

The silver halide grains obtained contained {110} planes as well as {111} planes.

We claim:

1. A photographic material containing silver chloride and/or silver chlorobromide grains that have {110} crystal planes and that are dispersed in a binder.

2. A photographic material according to claim 1, wherein the binder is a film-forming hydrophilic colloid.

3. A photographic material according to claim 2, wherein said binder is gelatin.

4. A photographic material according to claim 1, wherein the silver chlorobromide grains contain at most 90 mole percent of bromide.

5. A photographic material according to claim 1, wherein said grains are present in a hydrophilic colloid layer of a silver halide emulsion material that can be developed and processed by means of aqueous liquids.

6. A photographic material according to claim 1, wherein the grains have a regular rhombododecahedral shape.

7. A photographic material according to claim 1, wherein the grains are spectrally sensitized.

8. A method of preparing a photographic silver halide emulsion containing silver chloride and/or silver chlorobromide grains, wherein the formation by precipitation of said grains and/or the growth of said grains is carried out in an aqueous medium in the presence of a protective hydrophilic colloid and at least one substance that when incorporated in an aqueous solution containing methylene blue dye partly in its aggregated and partly in its monomeric (non-aggregated) form enhances the intensity of the absorption band characteristic for the non-aggregated dye and acts to control the crystal habit and promote the {110} crystal habit of silver chloride or silver chlorobromide grains.

9. A method of preparing a photographic silver halide emulsion according to claim 8, wherein the silver chloride or silver chlorobromide is prepared by the single jet method and the substance controlling the crystal habit is present in the solution containing the chloride ions or a mixture of chloride and bromide ions in which the silver ion solution is injected.

10. A method of preparing a photographic silver halide emulsion according to claim 9, wherein in a first stage silver chloride nuclei are prepared and only in the further course of precipitation the substance controlling the crystal habit is added to the solution containing chloride ions or the mixture of chloride and bromide ions.

11. A method of preparing a photographic silver halide emulsion according to claim 8, wherein the silver halide is prepared by the double jet method.

12. A method of preparing a photographic silver halide emulsion according to claim 8, wherein the substance controlling the crystal habit is used in amounts varying between about 10 millimole and about 50 millimole per mole of silver chloride to be formed.

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