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

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

# (54) Precipitation of silver halide crystals comprising iodide.

(57) A method is disclosed for the preparation of a silver halide crystals comprising iodide in an amount of up to 3 mole % in the lattice of said crystals comprising the step of reacting a silver salt solution with a metal halide solution in the presence of at least one organic compound releasing iodide represented by the formula:

A-L-I

wherein A represents a group with a positive Hammett $\sigma_p$ value, and L is a divalent linking group.

A photographic material is further disclosed comprising a support and at least one silver halide emulsion layer on at least one side of said support coated from an emulsion containing silver iodohalide crystals prepared according to the method described hereinbefore. Moreover a method is described for the processing of said photographic material within a processing time of less than 50 seconds by the steps of developing, fixing, rinsing and drying.

Rank Xerox (UK) Business Services
(3.10/3.09/3.3.4)

## 1. Field of the invention.

The present invention relates to the preparation of silver halide emulsions, to X-ray silver halide photographic materials in which the said emulsions can be used and to the processing of said materials.

## 2. Background of the Invention

As it becomes more and more important in medical X-ray diagnosis for the exposed and processed films to become available to the examiner as soon as possible, there is a stringent demand for films suitable for rapid processing applications, also with respect to concurrent electronic systems. This can be translated as a requirement for rapid developability or high intrinsic sensitivity of the silver halide crystals, and further for providing images with a good image quality, having a neutral image tone, i.e. without dye stain.

Intrinsic sensitivity may be enhanced e.g. by enriching the iodide content of silver halide crystals to a certain extent. Moreover an enhanced amount of iodide will offer the possibility to get a better adsorption of certain spectral sensitizer. However dye stain may become more important and the development may be inhibited as the lower solubility may make the kinetics of development and fixation decrease. This occurs in particular in rapid processing conditions due to the very short development, fixing and rinsing times which do not allow the total destruction and/or rinsing out of those sensitizing or non-sensitizing dyes.

The way in which iodide ions have been built into the crystal volume and more particularly in the vicinity of and/or at the crystal surface is very critical to get a suitable compromise between high sensitivity (as a result of intrinsic sensitivity of the silver halide crystal and improved adsorption of spectral sensitizer) and rapid processability.

Already in the nucleation phase during silver halide precipitation a problem arises when iodide ions are present in the reaction vessel or into the halide solution feeding system. Due to its low solubility, silver iodide crystals are formed more quickly than silver halide crystals having other compositions. The efficiency with which the so-called "micromixing" proceeds in the reaction vessel with central stirring means during precipitation is insufficient. As a consequence it is nearly impossible to reach a homogenous halide distribution in the initially, quickly formed nuclei. As the said silver iodide crystals further take part in Ostwald ripening and recrystallisation processes during precipitation, it is impossible to determine exactly where and how much iodide ions are built in at predetermined sites into the volume or at the surface of the thus formed silver halide crystal.

A solution to provide a more homogenous micromixing has been found by the preparation of the initial nuclei in a reaction vessel that is smaller and separated from the bulk vessel as has e.g. been described in DE 1 472 745, DE 2 116 157 and DE 2 556 885, in US-Patents Nos. 3,705,034; 4,334,012; 4,336,328; 4,684,607 and 5,004,679 as well as in EP-Applications Nos. 326 852, 326 853, 370 116, 407 576, 355 535, 408 752, 368 275, 374 852, 374 853, 374 954. The formation of initial nuclei in a small separate reaction vessel is followed by growth of the said initial nuclei by means of further single or double jet precipation but also by means making use of the Ostwald ripening technique wherein the driving force for growing the silver halide crystals is the difference in crystal diameter between the initial nuclei and the added "feeding crystals" and/or the differences in solubility between both types of crystals. In another embodiment it is also possible to grow the initial crystals, also called "nuclei", by Ostwald ripening in the reaction vessel, being separated from the vessel where the said nuclei are formed. Growth may occur by a difference in pAg between those two separated vessels, so that the dissolution step is fully determining the way in which silver iodide may be built in.

Nevertheless uneven growth of the small nuclei due to their unstability and accumulation of silver halide deposit due to insufficient protection by the protective colloid is bringing about technological complications during the preparation of silver halide crystals containing iodide. Consequently the improvement with respect to sensitivity enhancement and/or dye stain reduction in rapid processing applications is insufficient when the previously described techniques are applied.

## 3. Objects of the invention.

Therefor it is an object of this invention to prepare silver halide crystals with enhanced amounts of iodide ions in favour of sensitivity and providing good adsorption of spectral sensitizer, overcoming the disadvantages of unacceptable loss in developability, and dye stain in rapid processing applications.

Other objects will become apparent from the description hereinafter.

## 4. Summary of the invention

In accordance with the present invention a method is disclosed for the preparation of a silver halide crystals comprising iodide in an amount of up to 3 mole % in the lattice of said crystals comprising the step of reacting a silver salt solution with a metal halide solution in the presence of at least one organic compound releasing iodide represented by the formula:

A-L-I (I)

wherein A represents a group with a positive Hammett $\sigma_p$ value, commonly known as an electron-accepting or electon-withdrawing group, and L is a divalent linking group.

Further in accordance with this invention a photographic material is disclosed comprising a support and at least one silver halide emulsion layer on at least one side of said support coated from an emulsion containing silver iodohalide crystals prepared according to the method described hereinbefore.

Moreover a method is described for the processing of said photographic material within a processing time of less than 50 seconds by the steps of developing, fixing, rinsing and drying.

## 5. Detailed description of the invention

According to this invention it has been found to prepare silver iodohalide crystals by reacting a silver salt solution with a metal halide solution in the presence of at least organic agent releasing iodide.

The use of organic halide releasing compounds is not new in the photographic art. In Zh. Nauch. Prikl. Fot. Kine 35, 142, (191), Poloznikov and Shapiro describe new forms of silver bromide microcrystals as a result of the interaction of silver nitrate and bromoacetic acid. JP-A-02-68538 describes the use of organic chloride, bromide and iodide slow releasers to avoid microscopic heterogeneities inherently associated with non-homogeneous concentrations of silver ions and halide ions in the conventional circumstances of nucleation and growth. Examples of such heterogeneities include heterogeneous particle size, crystal irregularities and heterogeneous halide distribution between and within particles. Further extensions of this teaching can be found in EP 0 341 728 and EP 0 531 799.

In the general formula "A-L-I" A is an electron-accepting or electron withdrawing, also called a group with a positive Hammett $\sigma_p$-Hammett value. Hammett $\sigma_p$ values have been defined e.g. on p. 96 of "Structure/Activity Correlations for Drugs" published by Nankodo (1979).

Examples of electron witdrawing groups are -COOH, $-SO_2R$, $-SO_3R'$, etc. wherein R represents a substituted or unsubstituted aliphatic or aromatic group and R' represents an inorganic cation or an organic cationic group.

Most preferred A groups include a carboxylic acid group, a cyano group, a carbamoyl group, an acyl group, a sulphonyl group, an oxycarbonyl group, a sulphamoyl group.

The organic compounds releasing iodide are preferably corresponding to the above formula wherein the divalent linking group is chosen from unsubstituted or substituted alkylene, unsubstituted or substituted oxyalkylene, unsubstituted or substituted aralkylene, or combinations of two or more thereof, wherein several atoms of L, or of A and L, can combine to form a ring, and wherein the iodine atom is not bound to an aromatic moiety or to an atom bearing a double bond, or to a hetero-atom.

Useful examples of such iodide ion slow releasers include following compounds :

$ICH_2COOH$ (I-1)

$I(CH_2)_2COOH$ (I-2)

$I(CH_2)_3COOH$ (I-3)

$CH_3CHICOOH$ (I-4)

$CH_3CH_2CHICOOH$ (I-5)

$CH_3CHICH_2COOH$ (I-6)

HOOC-CHI-COOH (I-7)

$HOOC-CH_2-CHI-COOH$ (I-8)

$ICH_2CN$ (I-9)

$I(CH_2)_2CONH_2$ (I-10)

$ICH_2COCH_3$ (I-11)

$I(CH_2)_2SO_2CH_3$ (I-12)

$ICH_2COOCH_3$ (I-13)

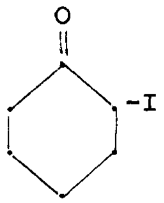
$ICH_2CH_2SO_3Na$ (I-14)

$ICH_2CONH_2$ (I-15)

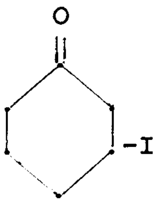
$ICH_2-CO-NH-C(CH_2OH)_3$ (I-16)

$ICH_2-CO-NH-C_2H_4-SO_3Na$ (I-17)

$ICH_2-CO-NH-CH_2-(CHOH)_4-CH_2OH$ (I-18)



(I-19)



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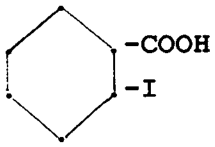

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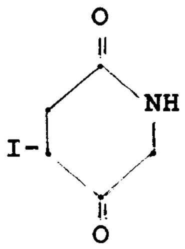

(I-22)

In a particular preferred embodiment the iodide ion slow releaser is simply mono-iodoacetic acid (I-1).

The choice of a compound releasing iodide ions is mainly determined by its activity observed in real circumstances. E.g. the pH value of the medium and the presence of highly active nucleophilic ions have an important role therein. The iodide releaser is preferably used in aqueous solution in a concentration between 0.1 and 1 molar.

Suitable preparation methods for silver iodiohalide crystals that may be applied, partially in the presence of organic releasers containing iodide according to this invention, are described e.g. by T.H. James in "The Theory of the Photographic Process", 4th edition (Macmillan, 1977); P. Glafkides in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", the Focal Press, London (1966), and V.L. Zelikman et al. in "Making and Coating Photographic Emulsion", The Focal Press, London (1966).

Before or during the emulsion crystal preparation step a preferred compound present in the precipitation vessel is ammonia.

The emulsions according to this invention can be prepared by the known methods like the single-jet method, wherein a iodohalide salt solution can be added to the solution containing a protective colloid in the reaction vessel before the start of the precipitation. A silver salt solution can be added during a predetermined time while stirring. Iodide ions may be distributed in a homogenous or heterogenous way over the silver iodohalide volume. E.g. a core-shell structure is typical for a crystal structure with a heterogenous distribution over its crystal volume. In order to obtain such a core-shell structure with at least one shell a (iodo)halide containing solution may consecutively be added to the reaction vessel after addition of a silver salt solution. This consecutive addition may be repeated in the presence of at least one organic compound releasing iodide in order to obtain different internal shell(s) containing silver iodide built up around the core. The core may be rich or poor in iodide ion concentration or may even be iodide free provided that at the start of the precipitation no iodide ions are present in the reaction vessel. The silver iodohalide crystals thus formed may have an outermost shell with a lower or a higher iodide concentration in comparison with an adjacent shell, depending on the precipitation conditions.

The size distribution of the silver halide particles prepared according to this invention may be homodisperse or heterodisperse. Homodisperse distributions are obtained when 95 % of the grains have a size that does not deviate for more than 30 % from the average grain size. Average particle size diameters may vary over a wide range e.g. from 0.1 to 2.0 µm.

In some applications it may be advantagous to get narrow particle size distributions as e.g. in applications requiring high gradations. In that case it is more preferable to apply the double-jet technique wherein a protective colloid solution is added to the reaction vessel before and wherein solutions of silver salts and halide salts are added simultaneously. The silver halide composition may be varied during the additions and especially when shells obtained by conversion with iodide ions are present, a combination of single and double jet precipitation techniques may be useful. Due to the lower solubility of silver iodide in comparison with silver bromide or silver chloride, said iodide ions are namely able to displace bromide and/or chloride ions from the grain, a technique known in the art as conversion. The said conversion step can also be performed at the silver halide crystal surface.

A further precipitation technique may be the triple-jet technique to enhance the possibility to vary the halide composition in the volume of the crystals during precipitation. Combinations of single-jet, double-jet and triple-jet precipitation techniques are possible.

It is clear that according to this invention in each specific embodiment iodide ions that are incorporated in the lattice of iodohalide crystals during precipitation are released from at least one organic compound releasing iodide ions. It may be useful to replace the said organic compound(s) partially by an inorganic iodide salt if required e.g. from kinetic considerations during precipitation.

For each precipitation according to this invention variable concentrations of solutions providing respectively silver and halide ions may be used during the different precipitation steps. Variable flow rates for the said solutions may be available during precipitation while controlling the pAg value and the temperature in the reaction vessel.

In another embodiment it is possible to prepare the initial nuclei in a separate reaction vessel as has e.g. been described in EP-Application 326 852.

During precipitation a problem may arise in that the volume in the vessel continuously increases and in that the amount of halide ions makes the ionic strength to increase tremendously. This problem may be overcome by making use of an ultrafiltration unit coupled to the reaction vessel, to precipitate the silver halide crystals containing iodide at a constant vessel volume or at a constant ionic strength. Ultrafiltration can be applied not only during but also after the precipitation step.

The silver halide particles of the photographic emulsions according to the present invention may further have a regular crystalline form, e.g. cubic or octahedral or a transition form. Also an irregular crystalline form such as a spherical form or a tabular form may be obtained. Otherwise the emulsion crystals may have a composite crystal form comprising a mixture of said regular and irregular crystalline forms.

The crystals may be doped with whatever a dope, as e.g. with $Rh^{3+}$, $Ir^{4+}$, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$.

In accordance with this invention the halide composition is chloroiodide, chlorobromoiodide or bromoiodide.

The amount of iodide at certain sites within the crystal volume can vary between wide limits. Preferably not more than 30 mole % of iodide ions and more preferably not more than 10 mole % are built in locally and in accordance with this invention not more than 3 mole % ions of iodide ions are built in over the whole silver halide crystal volume of the grains.

In accordance with this invention cubic or tabular silver (chloro)bromoiodide or chloroiodide are preferred.

Before or during precipitation chemical and/or spectral sensitizers can be added to the emulsion vessel. Further during precipitation grain growth restrainers or accelerators may be added.

The most commonly used protective colloid in the reaction vessel at the start of the precipitation is gelatin which is a thermoreversible polymer, showing a sufficient gel strength after coating. Conventional lime-treated or acid treated gelatin can be used. The preparation of such gelatin types has been described in e.g. "The Science and Technology of Gelatin", edited by A.G. Ward and A. Courts, Academic Press 1977, page 295 and next pages. The gelatin can also be an enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966). Other types of protective colloids for use instead of or in addition to gelatin include various natural film-forming substances and synthetic resins, e.g. polyoxyethylene glycols, polyvinylpyrrolidone, starch and starch derivatives and colloidal silica. In EP-Application 392 092 it has e.g. been shown to use silica sol as a protective colloid in the preparation of silver halide emulsions.

After precipitation, the emulsion has to be coagulated and washed if no ultrafiltration technique is used before. Coagulation in gelatineous medium can e.g. be effected by an alcohol or a salt or if the emulsion contains a sufficient amount of acid-coagulable gelatin derivatives or hydrogen bridge forming anionic polymeric compounds by addition of an acid to lower the pH value to the isoelectric point. Well-known examples of hydrogen bridge forming anionic polymeric compounds are polystyrene sulphonic acid and sulphonated copolymers of styrene, which are commonly used. Acid coagulable gelatin derivatives as phtaloyl or N-phenyl carbamoyl gelatin can be used, requiring only adjustment of the pH to the right value to cause the emulsion to coagulate.

Suitable coagulation techniques have been described e.g. in U.S. Patent Specifications 2,614,928; 2,614,929 and 2,728,662. The silver halide emulsions can be precipitated in silica medium in the presence of a compound releasing iodide whereupon it is possible to apply the flocculation method as described in EP-A 517 961.

Separately formed two or more different silver halide emulsions may be mixed for use in silver halide photographic materials in accordance with the present invention.

The light-sensitive silver halide emulsion prepared according to the present invention can be chemically sensitized as described i.a. in the above-mentioned "Chimie et Physique Photographique" by P. Glafkides, in the above-mentioned "Photographic Emulsion Chemistry" by G.F. Duffin, in the above-mentioned "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 rhodanines. The emulsions can be sensitized also by means of gold-sulphur ripeners or by means of reductors e.g. tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. Chemical sensitization can also be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitization methods or a combination thereof can be used. A mixture can also be made of two or more separately precipitated emulsions being chemically sensitized before mixing them.

Before, during or after chemical sensitization spectral sensitizer(s) may be added to the redispersed silver halide emulsion. This may 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 sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, 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 the already cited Research Disclosure Item 22534. Especially preferred green sensitizer in connection with the present invention are anhydro-5,5'-dichloro-3,3'-bis-(n.sulfobutyl)-9-ethyloxacarbo-cyanine hydroxide and anhydro-5,5'-dichloro-3,3'-bis(n.sulfopropyl)-9-ethyloxacarbo-cyanine hydroxide.

In classical emulsion preparation spectral sensitization traditionally follows the completion of chemical sensitization. However, especially in connection with tabular grains having a large specific surface, it is specifically considered that spectral sensitization may occur simultaneously with or may even precede completely the chemical sensitization step: the chemical sensitization after spectral sensitization is believed to occur at one or more ordered discrete sites of tabular grains. This may also be done with emulsions, wherein the chemical sensitization proceeds in the presence of one or more phenidone and derivatives, a dihydroxy benzene as hydroquinone, resorcinol, catechol and/or a derivative(s) therefrom, one or more stabilizer(s) as e.g. 1-p-carboxyphenyl, 4,4' dimethyl-3-pyrazolidine-1-one, auxiliary agent(s) or antifoggant-(s), one or more spectal sensitizer(s) or combinations of said ingredients

Other dyes, which per se do not have any spectral sensitization activity, or certain other compounds, which do not substantially absorb visible radiation, can have a supersensitization effect when they are incorporated together with said spectral sensitizing agents into the emulsion. Suitable supersensitizers 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.

To the silver halide emulsion prepared in accordance with the present invention may be added compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of 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 i.a. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercaptotetrazole, 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-A 1,203,757, GB-A 1,209,146, JA-Appl. 75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US-A 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid, 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), Chaptre VI.

The fog-inhibiting agents or stabilizers can be added to the silver halide emulsion prior to, during, or after the chemical ripening thereof and mixtures of two or more of these compounds can be used.

The silver halide emulsions prepared in accordance with the present invention can be used to form one or more silver halide emulsion layers coated on a support to form a photographic silver halide element according to well known techniques.

The photographic element of the present invention may 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, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g higher contrast, sensitization, and development acceleration.

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-A 3,038,805

- 4,038,075 - 4,292,400.

The photographic element of 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, hardeners, and plasticizers as described below.

The gelatin binder of the photographic elements can be forehardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. divinyl-sulphonyl-methane, ethylene di-(vinyl-sulphone), 1,3-vinylsulphonyl-2-propanol, bis-(vinylsulphonyl-methyl)-ether, 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 as 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 Patent 4,063,952 and with the onium compounds as disclosed in EU Patent Application 408,143.

The emulsion may be coated on any suitable substrate such as, preferably, a thermoplastic resin e.g. polyethyelenterephtalate or a polyethylene coated paper support.

If, however, (an) additional protective colloid(s) is (are) present during the precipitation or added during or after redispersion, then suitable additives for improving the dimensional stability of the photographic element may be added, i.a. 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.

Plasticizers suitable for incorporation in the emulsions according to the present invention are e.g. glycol, glycerine, or the latexes of neutral film forming polymers including polyvinylacetate, acrylates and methacrylates of lower alkanols, e.g. polyethylacrylate and polybutylmethacrylate.

Suitable UV-absorbers are i.a. aryl-substituted benzotriazole compounds as described in US-A 3,533,794, 4-thiazolidone compounds as described in US-A 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A 3,705,805 and 3,707,375, butadiene compounds as described in US-A 4,045,229, and benzoxazole compounds as described in US-A 3,700,455.

In general, the average particle size of spacing agents is comprised between 0.2 µm and 10 µm. 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 i.a. 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-A 4,614,708.

The photographic silver halide emulsions prepared according to the present invention can be used in various types of photographic elements such as i.a. in photographic elements for graphic arts and for so-called amateur and professional photography, diffusion transfer reversal photographic elements, low-speed and high-speed photographic elements, colour materials, X-ray materials, materials for micrographic applications etc.. In a preferred embodiment the said photographic silver halide emulsions are used in single side or double side coated X-ray materials.

The photographic element with (an) emulsion(s) according to the present invention may contain one single emulsion layer, as it is the case for many applications, or it can be built up by two or even more emulsion layers. In X-ray photography a material with a single or a duplitized emulsion layer coated on one or both sides of the support may contain silver halide emulsions according to this invention. By using duplitized emulsions differing in photographic speed by at least 0.15 log E a gain in cross-over in double side coated materials can be obtained. In the case of color photography the material contains blue, green and red sensitive layers each of which can be single coated, but merely consist of double or even triple layers.

The photographic material can contain several non-light sensitive layers, e.g. an antistress topcoat 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 used in these intermediate layers are described in e.g. US Patents 4,092,168, US 4,311,787, DE 2,453,217, and GB Patent 7,907,440. By the use of dyes in such an intermediate layer between the emulsion layers and the support there will be only a small negligable loss in sensitivity but in rapid processing conditions decolouration of the filter dye layers may form a problem. Therefor it should be recommended to decrease the thickness of the whole coated layer packet. Moreover this results in shorter drying times in the processing cycle.

One or more backing layers can be provided at the non-light sensitive side of the support of materials coated with at least one emulsion layer at only one side of the support. These layers which can serve as anti-curl layer can contain e.g. matting agents like silica particles, lubricants, antistatic agents, light absorbing dyes, opacifying agents, e.g. titanium oxide and the usual ingredients like hardeners and wetting agents.

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

The photographic material with silver halide grains prepared according to the present invention can be image-wise exposed by any convenient radiation source in accordance with its specific application.

Of course processing conditions and composition of processing solutions are dependent from the specific type of photographic material in which the silver iodohalide grains prepared according to the present invention are applied. For example, in a preferred embodiment of materials for X-ray diagnostic purposes said materials may be adapted to rapid processing conditions. Preferably an automatically operating processing apparatus is used provided with a system for automatic regeneration of the processing solutions. The forehardened material may be processed using one-part package chemistry or three-part package chemistry, depending on the processing application determining the degree of hardening required in said processing cycle. Further the developing and/or fixing step may proceed in hardener free processing solutions and replenishment of the developer and/or fixer solution may proceed by concentrate regeneration.

Applications within total processing times of 30 seconds and lower up to 90 seconds, known as common praxis, are possible. In accordance with this invention especially total processing times of less than 50 seconds comprising the steps of developing, fixing, rinsing and drying are preferred.

From an ecological point of view it is even possible to use sodium thiosulphate, partially or totally, instead of ammonium thiosulphate.

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

## 6. EXAMPLES

In the following examples the following solutions were used during the precipitation:

Solution 1: 1.5 liter of an aqueous solution containing 500 grams of silver nitrate.

Solution 2: 1.5 liter of an aqueous solution containing 350 grams of potassium bromide.

Solution 3 : 1.5 liter of an aqueous solution containing 345 grams of potassium bromide and 7.3 grams of potassium iodide.

Solution 4: 1.5 liter of an aqueous solution containing 339 grams of potassium bromide and 14.6 grams of potassium iodide.

Solution 5: 1.5 liter of an aqueous solution containing 333 grams of potassium bromide and 21.9 grams of potassium iodide.

Solution 6: 0.3 M of monoiodoacetic acid, brought to pH = 6.0 with sodium hydroxyde.

Solution 7: 1.4 liter of an aqueous solution containing 350 grams of potassium bromide.

Solution 8: 1.3 liter of an aqueous solution containing 350 grams of potassium bromide.

Solution 9: 1.2 liter of an aqueous solution containing 350 grams of potassium bromide.

### EXAMPLE No. 1.

Comparative emulsion No. 1:

Nucleation step:

61.0 ml of solutions 1 and 2 were introduced into a reaction vessel in 28 seconds using the double jet technique. Said reaction vessel initially contained 2.16 liter of destilled water at 45 °C, 12.6 grams of potassium bromide and 12.5 grams of gelatin. After one minute the reaction temperature of this mixture was raised to 70 ° C in 20 minutes and 47.5 grams of phthalated gelatin in 475 ml destilled water were added. After 10 minutes the neutralization step was started.

First neutralization step:

20.3 ml of solution 1 were added to the reaction vessel at a rate of 7.5 ml per minute to reach a pBr value of 1.63, whereafter the first growth step was started.

First growth step:

A double jet precipitation was started using solutions 1 and 2 which continued for 40 minutes 51 seconds. During this precipitation, the pBr value was kept constant at 1.63. The flowing rate of solution 1 was 7.5 ml per minute at the start, linearly increasing to 22.2 ml per minute at the end of the precipitation. Thereafter the second neutralisation phaze was started.

Second neutralization step:

45.8 ml of solution 1 was added at a rate of 7.5 ml per minute so that a pBr of 2.77 was obtained. The precipitation was then continued by a second growth step.

Second growth step (during which 62.0 mole % of the total amount of $AgNO_3$ was used):

930 ml of solution 1 was injected in the reaction vessel at a rate of 7.5 ml per minute at the start linearly increasing to 37.5 ml per minute at the end of the precipitation. The pBr was kept constant at 2.77 using solution 3.

Comparative emulsion No. 2:

The same procedure was followed as that for the comparative emulsion No. 1, with the only difference that in the second growth step solution 4 was used instead of solution 3.

Comparative emulsion No. 3:

The same procedure was followed as that for the comparative emulsion No. 1, with the only difference that in the second growth step solution 5 was used instead of solution 3.

Inventive emulsions

For the preparation of inventive emulsions Nos. 1 to 3 the triple jet technique was applied, wherein the solutions 1, 2, 6, 7, 8 and 9 were used.

Inventive emulsion No. 1:

This emulsion was prepared in the same way as comparative emulsion No. 1 with the only difference that after the second neutralization step 100 ml of solution 6 were added to the reaction vessel and that in the second growth step solution 7 was used instead of solution 3.

Inventive emulsion No. 2:

This emulsion was prepared in the same way as inventive emulsion No. 1 with the only difference that after the second neutralization step 200 ml of solution 6 were added to the reaction vessel and that in the second growth step solution 8 was used instead of solution 7.

Inventive emulsion No. 3:

This emulsion was prepared in the same way as inventive emulsion No. 1 with the only difference that after the second neutralization step 300 ml of solution 6 were added to the reaction vessel and that in the second growth step solution 9 was used instead of solution 7.

The emulsions the preparation of which has been described hereinbefore were futher coated as follows:

Washing and dispersing procedure.

After the emulsion precitation was ended the pH value was lowered to 3.5 with diluted sulphuric acid and the emulsion was washed using demineralized water of 11 °C. At 45 °C 160 grams of gelatin were added and the values of pH and pAg at 40 °C were adjusted to 5.5 and 8.15.

Sensitization

Emulsions Nos. 1 to 3 (comparative and inventive emulsions) were each optimally sulphur and gold sensitized in the presence of sodium thiocyanate and anhydro-5,5'-dichloro-3,3'-bis(n.sulfobutyl)-9-ethyloxacarbo-cyanine hydroxide in an amount of 660 mg per mole of silver nitrate.

Emulsion Coating.

Each emulsion was stabilized with 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and after addition of the normal coating additives the solutions were coated simultaneously together with a protective layer on both sides of a polyethylene terephthalate film support having a thickness of 175 µm. The resulting photographic material contained per side an amount of silver halide corresponding to 3.5 grams of $AgNO_3$ per $m^2$.

For the protective layer, the coating weight expressed in grams per square meter per side was 1.1 g of gelatin, 0.023 g of polymethylmethacrylate having a mean particle size of 3.5 µm and 0.1 g of formaldehyde as a hardening agent.

Exposure,sensitometric and densitometric data:

Samples of these coatings were exposed with green light of 540 nm during 0.1 seconds using a continuous wedge and were processed during the 38 seconds cycle described below. The density as a function of the light dose was measured and therefrom were determined the following parameters:

- fog level F (with an accuracy of 0.001 density),
- the speed S (in log E(xposure)) at a density of 1 above fog: every decrease of the value of S with 0.30 units corresponds with an enhancement of the sensitivity with a factor 2,
- the contrast GRAD, calculated between the densities 0.25 and 2.0 above fog.

Further, absorption spectra were registrated after processing and absorption values were measured at 545 nm and 500 nm respectively, corresponding to the absorption maxima of the dye adsorbed at the silver halide crystal surface and in the gelatin matrix.

Conditions for the 38 seconds processing as applied in accordance with this invention:

- processing machine : CURIX HT530 (Agfa-Gevaert trademarked name) with the following time (in seconds) and temperature (in °C) characteristics:

| | |
|---|---|
| loading | 0.2 sec. |
| developing | 9.3 sec. 35 °C in developer I described below |
| cross-over | 1.4 sec. |
| rinsing | 0.9 sec. |
| cross-over | 1.5 sec. |
| fixing | 6.6 sec. 35 °C in fixer I described below |
| cross-over | 2.0 sec. |
| rinsing | 4.4 sec. 20 °C |
| cross-over | 4.6 sec. |
| drying | 6.7 sec. |
| total | 37.6 sec. |

Composition of the developer:

- concentrated part ready-for-use:

| | |
|---|---|
| water | 200 ml |
| potassium bromide | 12 grams |
| potassium sulphite (65% solution) ethylenediaminetetraacetic acid, | 249 grams |
| sodium salt,trihydrate | 9.6 grams |
| hydroquinone | 106 grams |
| 5-methylbenzotriazole | 0.076 grams |
| 1-phenyl-5-mercaptotetrazole | 0.040 grams |
| sodiumtetraborate (decahydrate) | 70 grams |
| potassium carbonate | 38 grams |
| potassium hydroxide | 49 grams |
| diethylene glycol | 111 grams |
| 4-hydroxymethyl-4methyl-1phenyl-3-pyrazolidinone | 5.9 grams |
| Water to make 1 liter<br>pH adjusted to 11.15 at 25 °C with potassium hydroxide. | |

For initiation of the processing one part of the concentrated developer was mixed with 3 parts of water.
No starter was added.
The pH of this mixture was 10.30 at 25 °C.

Composition of the fixer ready-for-use:

- concentrated part :

| | |
|---|---|
| sodium thiosulfate decahydrate | 628 grams |
| sodium sulphite | 40 grams |
| boric acid | 36 grams |
| citric acid monohydrate | 40 grams |
| water to make 1 liter<br>pH adjusted with sodium hydroxyde to 6.60 at 25 °C | |

To make this fixer ready for use one part of this concentrate was mixed with 1 part of water. A pH of 6.78 was measured at 25 °C.
In Table I the following data are summarized:

- iodide content: theoretical amount of $[I^-]$ present in mole% and real amount present as determined by X-ray fluorescence spectroscopy (XRF)
- average diameter $d_M$ of the crystals determined from volume measurement of the tabular grain by electrochemical reduction of the silver ions in the crystal lattice and calculating the diameter derived from the sphere having the same volume as the said tabular grain.
- average diameter $d_{EM}$ of the crystals determined from electron microscopic measurements.
- average thickness d of the crystals determined from electron microscopic measurements.
- average aspect ratio AR as the ratio of average thickness d and average diameter $d_{EM}$.

Table I

| Sample No. | [I⁻] | XRF | $d_M$ | $d_{EM}$ | d | AR |
|---|---|---|---|---|---|---|
| Comp. 1 | 1 | 1.0 | 0.71 | 1.18 | 0.17 | 6.8 |
| Comp. 2 | 2 | 1.8 | 0.71 | 1.19 | 0.17 | 7.0 |
| Comp. 3 | 3 | 2.9 | 0.72 | 1.28 | 0.15 | 8.4 |
| Inv. 1 | 1 | 0.9 | 0.72 | 1.12 | 0.19 | 5.6 |
| Inv. 2 | 2 | 1.7 | 0.75 | 1.28 | 0.17 | 7.5 |
| Inv. 3 | 3 | 2.8 | 0.86 | 1.40 | 0.22 | 6.4 |

From Table I it can be derived that iodide liberated from a compound releasing iodide as monoiodoacetic acid is built-in in the crystal lattice as quantitatively as iodide from halide salt solutions. The crystal distributions obtained are fully comparable with each other as is clear from electron microscopic measurements and electrochemically performed volume measurements.
Sensitometric and densitometric data measured as described hereinbefore are summarized in Table II.

Tabel II

| Sample No. | [I⁻] | F | S | GRAD | $D_{max}$ | $A_{500}$ | $A_{545}$ |
|---|---|---|---|---|---|---|---|
| Comp. 1 | 1 | 0.034 | 1.65 | 2.87 | 3.459 | 0.04 | 0.03 |
| Comp. 2 | 2 | 0.031 | 1.59 | 2.26 | 3.249 | 0.11 | 0.06 |
| Comp. 3 | 3 | 0.125 | 1.98 | 1.59 | 2.876 | 0.14 | 0.32 |
| Inv. 1 | 1 | 0.031 | 1.68 | 3.38 | 3.828 | 0.02 | 0.02 |
| Inv. 2 | 2 | 0.004 | 1.47 | 3.03 | 3.157 | 0.04 | 0.03 |
| Inv. 3 | 3 | 0.059 | 1.84 | 1.52 | 2.523 | 0.10 | 0.19 |

As can be seen from table II the sensitivity as well as the gradation is obviously decreased when the iodide concentration in the silver bromoiodide crystals is enhanced. Moreover the enhanced residual stain after processing for the comparative emulsion with an iodide content of 2 mole % does not appear for the emulsion with the same iodide content according to this invention. Thanks to the incorporation of a higher iodide amount making use of a special iodide releasing organic compound it is possible to get a remarkably increased sensitivity and a low residual stain level after processing. However from a concentration of 3 mole % of iodide or higher the disadvantages like too low gradations and too high residual stain levels do appear again. Table II clearly illustrates that residual stain is remarkably lower if iodide ions have been built in the crystal lattice by means of an iodide releasing agent according to this invention.

EXAMPLE No. 2

Chemically sensitized fast monodisperse negative working silver bromoiodide emulsions having a varying iodide content were prepared in the following manner.

Comparative emulsion No. 4.

50 g of gelatin were added to 1.000 ml of demineralized water containing 15 g of methionin as a growth accelerator under constant stirring at 400 rpm. The mixture was held for 30 minutes at room temperature and heated up to 60 ° C. This temperature was kept constant during the entire precipitation process.

Before starting the precipitation a few drops of a diluted solution of potassium bromide were added so as to bring the pAg of the solution at a value of 7.9.

36.5 ml of 2.94 N $AgNO_3$ (3.65 mole % of the total amount of $AgNO_3$) were added under the following conditions. During the first five minutes the flow rate of $AgNO_3$ was kept constant at 7.3 ml/min. A 100%

KBr solution was added at a variable flow rate so as to keep the pAg constant at 7.9. During the following 40 minutes and 40 seconds the flow rate of $AgNO_3$ was steadily increased from 7.3 ml/min up to 15.5 ml/min whereas the pAg was kept constant at 7.9 by regulating the flow rate KBr solution, allowing 463.5 mi of $AgNO_3$ to be added.

To make an emulsion having a core shell structure, the next 500 ml of silver nitrate were added at an increasing flow rate going from 15.5 ml/min. to 21.0 ml/min. The pAg was kept constant at the same value of 7.9 as for the core precipitation, but the halide composition was changed from a 100% KBr composition to a composition of 98 mole % KBr and 2 mole % KI for the shell. Over the whole silver bromoiodide crystal an average amount of 1 mole % of iodide ions was incorporated in this way.

After five minutes the pH of the emulsion was reduced from 5.8 to 3.5 by adding a sufficient quantity of 6N of sulfuric acid.

Hereupon the conventional treatment processes such as washing and redispersing were applied to the emulsion: pAg was adjusted to a value of 8.4 at 45 ° C, pH to a value of 5.8. All of the obtained silver halide crystals had a cubic crystal habit and an average diameter of 0.64 $\mu$m was measured.

The redispersed emulsion was chemically sensitized for a period of 4 hours at 48 ° C in the presence of p-toluene thiosulphonate, sodium thiosulphate, sodium sulphite and a mixture of gold(III)-chloride and ammoniumthiocyanate so as to obtain an optimum in the relationship between fog and sensitivity.

The emulsion was spectrally sensitized with anhydro-5,5'-dichloro-3,3'-bis(n.sulfobutyl)-9-ethyloxacarbocyanine hydroxide in an amount of 375 mg per mole of silver halide and stabilized with 4-hydroxy-6-methyl-1,3,3a-tetrazaindene before coating on a polyester support of 175 $\mu$m thickness. The emulsion layers were coated at a ratio of 6.8g/m$^2$ of silver halide expressed as the equivalent amount of $AgNO_3$.

Comparative emulsion No. 5.

The whole precipitation, flocculation, redispersing and sensitization procedure was performed in the same way as for comparative emulsion No. 4, except for the presence of a mixture of 94 mole % KBr and 6 mole % KI that was added as a halide composition for the shell precipitation, so as to obtain an average iodide concentration over the core shell emulsion of 3 mole % of iodide.

Comparative emulsion No. 6.

The whole precipitation, flocculation, redispersing and sensitization procedure was performed in the same way as for comparative emulsion No. 4, except for the presence of a mixture of 88 mole % KBr and 12 mole % KI that was added as a halide composition for the shell precipitation, so as to obtain an average iodide concentration over the core shell emulsion of 6 mole % of iodide ions.

Inventive emulsion No. 4.

The whole precipitation, flocculation, redispersing and sensitization procedure was performed in the same way as for comparative emulsion No. 4, except for the presence instead of potassium iodide of monoiodoacetic acid in an equivalent amount as KI that was added so as to convert the silver bromide core after precipitation of 50 mole % of the total amount of silver nitrate. For the precipitation of the shell 100 mole % KBr was used to obtain a silver bromide shell. In this way an average amount of iodide ions equivalent to 1 mole % was built-in in the silver bromoiodide crystals of the core shell emulsion.

Inventive emulsion No. 5.

The whole precipitation, flocculation, redispersing and sensitization procedure was performed in the same way as for comparative emulsion No. 4, except for the presence instead of potassium iodide of monoiodoacetic acid in an equivalent amount as KI that was added so as to convert the silver bromide core after precipitation of 50 % of the total amount of silver nitrate. For the precipitation of the shell 100 mole % KBr was used to obtain a silver bromide shell. In this way an average amount of iodide ions equivalent to 3 mole % was built-in in the silver bromoiodide crystals of the core shell emulsion.

Inventive emulsion No. 6.

The whole precipitation, flocculation, redispersing and sensitization procedure was performed in the same way as for comparative emulsion No. 5, except for the presence instead of potassium iodide of monoiodoacetic acid in an equivalent amount as KI that was added so as to convert the silver bromide core after precipitation of 50 mole % of the total amount of silver nitrate. For the precipitation of the shell 100 mole % KBr was used to obtain a silver bromide shell. In this way an average amount of iodide ions equivalent to 6 mole % was built-in in the silver bromoiodide crystals of the core shell emulsion.

The different ways to build iodide ions in the lattice of the core shell emulsions described hereinbefore, respectively by coprecipitation of KI in the shell (comparative examples) and by conversion (inventive examples), were chosen so as to obtain practically equal halide profiles in the silver bromoiodide crystals. Said halide profiles were controlled by means of X-ray diffraction techniques.

The emulsions were chemically sensitized for a period of 4 hours at 48°C in the presence of p-toluene thiosulphonate, sodium thiosulphate, sodium sulphite and of a mixture of gold(III)-chloride and ammonium-thiocyanate. The emulsions were spectrally sensitized with anhydro-5,5'-dichloro-3,3'-bis(n.sulfobutyl)-9-ethyloxacarbo-cyanine hydroxide in an, amount of 375 mg per mole of silver halide and stabilized with 4-hydroxy-6-methyl-1,3,3a-tetrazaindene before coating on a polyester support of 175 $\mu$m thickness. The emulsion layers were coated with silver halide crystals at a ratio of 6.8g/m$^2$ of silver halide expressed as the equivalent amount of $AgNO_3$.

The photographic material samples were made by coating the emulsion on a polyethylene terephthalate support together with a composition for forming a protective gelatin layer. The amount of gelatin per square meter in the emulsion layers was 3.0 g, whereas in the protective layers it was 1.1 g.

Separate strips of the samples were subsequently exposed for the same exposure time to white light through a grey continuous wedge in a Herrnfeld Sensitometer and developed for 12 seconds in a developer having the following composition:

| | |
|---|---|
| hydroquinone | 30 g |
| 1-phenyl-pyrazolidine-3-one | 1.5 g |
| acetic acid 99 % | 9.5 ml |
| potassiumsulphite | 63.7 g |
| potassiumchloride | 0.8 g |
| EDTA-2Na | 2.1 g |
| potassium carbonate | 32 g |
| potassiummetabisulfite | 9 g |
| potassium hydroxyde | 14 g |
| diethyleneglycol | 25 ml |
| 6-methylbenztriazol | 0.09 g |
| glutardialdehyd 50% | 9.5 ml |
| 5-nitroindazole | 0.25 g |
| demineralized water to make 1 l. | |

The starter solution to be added had the following composition:

| | |
|---|---|
| acetic acid 99 % | 15.5 ml |
| KBr | 16 g |
| demineralized water up to 100 ml | |

Hereupon, the developed photographic strips were fixed in a conventional fixing bath comprising e.g. sodium thiosulfate and potassium metabisulfite, and then rinsed in water and allowed to dry.

Sensitometric properties of these film strips are given in table III. This table shows the sensitometric results in terms of fog, sensitivity (log E(xposure)) and overall contrast of the photographic strips prepared and exposed as set forth above and developed in the developing bath of the composition set forth above during an overall developing time of 12 seconds.

For the overall contrast the gradation is measured from the characteristic curve over a density range of 1.75 starting from a density value of 0.25 to 2.00 above fog.

In table III the following additional data are summmarized:

- iodide content: theoretical amount of [I$^-$] present in mole% and real amount present as determined by X-ray fluorescence spectroscopy (XRF)

- average diameter $d_M$ of the cubic core shell crystals determined from volume measurement of the grains by electrochemical reduction of the silver ions in the crystal lattice and calculating the diameter derived from the sphere having the same volume as the said cubic grain.
- absorption data at 500 nm and 545 nm, measured again after processing.

Table III

| Sample No. | $[I^-]$ | XRF | $d_M$ | F | S | GRAD | $A_{500}$ | $A_{545}$ |
|---|---|---|---|---|---|---|---|---|
| Comp. 4 | 1 | 1.0 | 0.61 | 0.037 | 2.21 | 3.96 | 0.057 | 0.076 |
| Comp. 5 | 3 | 2.7 | 0.59 | 0.046 | 2.29 | 3.82 | 0.089 | 0.238 |
| Comp. 6 | 6 | 5.2 | 0.64 | 0.091 | 2.29 | 2.71 | 0.095 | 0.433 |
| Inv. 4 | 1 | 1.0 | 0.65 | 0.041 | 2.18 | 4.09 | 0.041 | 0.050 |
| Inv. 5 | 3 | 2.7 | 0.65 | 0.038 | 1.98 | 3.78 | 0.054 | 0.107 |
| Inv. 6 | 6 | 4.9 | 0.63 | 0.055 | 2.06 | 1.21 | 0.076 | 0.386 |

From table III it can be derived that iodide liberated from an iodide releasing compound as monoiodoacetic acid is built-in in the crystal lattice as quantitatively as iodide from halide salt solutions. The crystal distributions obtained are fully comparable with each other as is clear from electron microscopic measurements and electrochemically performed volume measurements.

Especially with a concentration of 2 mole % of iodide ions, the differences with relation to fog and sensitivity for a comparable gradation are remarkable. This fully illustrates the advantages of emulsions wherefor an iodide releasing compound has been used to build in iodide ions. Moreover it is believed that due to an increased homogeneity the developablity is increased, resulting in an enhanced gradation.

Again the residual dye stain is systematically lower, as well for the materials coated with silver halide emulsion crystals containing less iodide ions as for the materials coated with silver halide emulsion crystals precipitated in the presence of a compound releasing iodide.

## Claims

1. Method for the preparation of silver halide crystals comprising iodide in an amount of up to 3 mole % in the lattice of said crystals comprising the step of reacting a silver salt solution with a metal halide solution in the presence of at least one organic compound represented by the formula:

   A-L-I (I)

   wherein A represents a group with a positive Hammett $\sigma_p$ value, and L is a divalent linking group.

2. Method according to claim 1 wherein said group A present in general formula (I) of said organic compound releasing iodide is chosen from the group consisting of a carboxylic acid group, a cyano group, a carbamoyl group, an acyl group, a sulphonyl group, an oxycarbonyl group, a sulphamoyl group.

3. Method according to claim 1 or 2, wherein the divalent linking group is chosen from unsubstituted or substituted alkylene, unsubstituted or substituted oxyalkylene, unsubstituted or substituted aralkylene, or combinations of two or more thereof, wherein several atoms of L, or of A and L, can combine to form a ring, and wherein the iodine atom is not bound to an aromatic moiety or to an atom bearing a double bond, or to a hetero-atom.

4. Method according to any of claims 1 to 3, wherein the said organic compound releasing iodide is mono-iodoacetic acid.

5. Method according to any of claims 1 to 4, wherein the reaction of the silver salt with the metal halide occurs in the presence of ammonia.

6. Method according to any of claims 1 to 5, wherein the said organic compound releasing iodide is present a metal halide solution thus forming a solution containing a mixed halide composition.

7. Photographic material comprising a support and at least one silver halide emulsion layer having silver halide crystals prepared according to the method of any of claims 1 to 6, wherein the silver iodohalide crystals are cubic or tabular silver (chloro)bromoiodide or chloroiodide crystals.

8. Photographic material according to claim 7 wherein said photographic material is a single side or double side coated X-ray material.

9. Method of processing a photographic material according to claim 7 or 8 wherein the processing proceeds within a processing time of less than 50 seconds by the steps of developing, fixing, rinsing and drying.

10. Method of processing a photographic material according to claim 9 characterized in that the developing and/or fixing step proceeds in hardener free processing solutions.

11. Method of processing a photographic material according to claim 9 or 10 wherein replenishment of the developer and/or fixer solution proceeds by concentrate regeneration.

**European Patent Office**

# EUROPEAN SEARCH REPORT

Application Number
EP 93 20 3040

## 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-A-0 561 415 (FUJI PHOTO FILM COMPANY LTD.)<br>* claims; compounds (1) - (5), (9), (10), (31) on p.5 - 12 * | 1-7 | G03C1/015<br>G03C5/16 |
| Y | | 8-11 | |
| X | EP-A-0 563 701 (FUJI PHOTO FILM COMPANY LTD.)<br>* claims; compounds (1) - (5), (9), (10), (31) on p.4 - 11 *<br>* table 3 * | 1-7 | |
| Y | | 8-11 | |
| Y | EP-A-0 542 354 (AGFA-GEVAERT N.V.)<br>* the whole document * | 8-11 | |
| D,Y | EP-A-0 341 728 (FUJI PHOTO FILM COMPANY LTD.)<br>* page 47, line 53 - page 48, line 13 * | 8 | |

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 | 18 April 1994 | Buscha, A |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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