⑲ **Europäisches Patentamt**
**European Patent Office**
**Office européen des brevets**

⑪ Publication number: **0 678 772 A1**

## ⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **95200651.8**

㉒ Date of filing: **17.03.95**

㉚ Priority: **06.04.94 EP 94200932**

㊸ Date of publication of application:
**25.10.95 Bulletin 95/43**

(84) Designated Contracting States:
**BE DE FR GB NL**

(51) Int. Cl.⁶: **G03C 1/005**

(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) Light-sensitive material comprising silver chlorobromoiodide or chloroiodide tabular grains.

(57) Emulsions are disclosed, comprising tabular silver chlorobromoiodide or silver chloroiodide tabular grains having (111) crystal faces, at least 75 mole % of chloride and up to 3 mole % of iodide, an average aspect ratio of at least 8:1, an average grain thickness of from 0.08 μm to less than 0.2 μm and wherein at least 50 % of the total projected area of all the grains is provided by said tabular grains. Said emulsions are very suitable for use in the light-sensitive layer(s) of a high sensitive photographic material comprising a support and on at least one side thereof at least one silver halide light-sensitive emulsion layer comprising said emulsions. Processing of such a photographic material is even possible in a total processing time of up to 38 seconds with low regeneration amounts in hardener-free processing solutions, without showing dye stain and with a suitable black image tone.

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

## FIELD OF THE INVENTION

The present invention relates to silver halide emulsions comprising tabular grains rich in chloride and to photographic materials containing such emulsions.

## BACKGROUND OF THE INVENTION

Tabular grains are known in the photographic art for quite some time. As early as 1961 Berry et al described the preparation and growth of tabular silver bromoiodide grains in "Photographic Science and Engineering, Vol 5, No 6". A discussion of tabular grains appeared in Duffin, Photographic Emulsion Chemistry, Focal Press, 1966, p. 66-72.

Early patent literature includes Bogg US-P 4,063,951, Lewis US-P 4,067,739 and Maternaghan US-P's 4,150,994; 4,184,877 and 4,184,878. However the tabular grains described herein cannot be regarded as showing a high diameter to thickness ratio, commonly termed aspect ratio. In a number of US-Applications filed in 1981 that became US-Patents in 1984 tabular grains with high aspect ratio and their advantages in photographic applications are described as, e.g., in US-P's 4,434,226; 4,439,520; 4,425,425; 4,425,426 and 4,433,048.

A survey on high aspect ratio silver halide emulsions appeared in Research Disclosure, Vol 225, Jan 1983, Item 22534.

High aspect ratio tabular grains exhibit several pronounced photographic advantages. Thanks to their particular morphology greater amounts of spectral sensitizers can be adsorbed per mole of silver halide if compared with classical globular grains. As a consequence such spectrally sensitized tabular grains show an improved speed-granularity relationship and a wide separation between their blue and minus blue speed. Sharpness of photographic images can be improved using tabular grains thanks to their lower light scattering properties again compared with conventional globular emulsion grains. In color negative materials the conventional sequence of the light sensitive-layers can be altered and the yellow filter layer can be omitted. In developed black-and-white images high covering power is obtained even at high hardening levels. Alternatively reduced silver halide coverages can be achieved if required, resulting again in improved sharpness. In double-side coated radiographic materials the presence of tabular grains reduces the so-called cross-over which is the dominant factor for sharpness in such materials.

In the refences on tabular grains cited above especially silver bromide or silver iodobromide emulsions having a high sensitivity are disclosed whereas the use of e.g. emulsions with tabular grains rich in chloride has hitherto been considered to be disadvantageous with respect to sensitivity. For emulsions with crystals rich in chloride, applications in the field of less sensitive materials as e.g. graphic arts materials, duplicating materials, radiographic hard-copy materials, diffusion transfer reversal materials and black-and-white or color print materials are well-known. The advantages of said emulsions with crystals rich in chloride regarding higher development and fixing rates, are highly appreciated.

As nowadays the tendency is present to get materials processed in shorter processing times, it would be highly appreciated to combine said advantages with a high sensitivity for application in high-sensitive materials.

## OBJECTS AND SUMMARY OF THE INVENTION

It is therefor an object of this invention to provide a silver halide emulsion comprising crystals rich in chloride, showing a high sensitivity.

It is a further object to provide silver halide photographic materials coated from such emulsions, providing a high sensitivity.

It is a still further object to process said photographic materials in a total processing time of up to 50 seconds with low regeneration amounts of hardener-free processing solutions, without leaving dye stain and with a suitable black image tone.

The objects described above have been accomplished by

- providing an emulsion containing silver chlorobromoiodide or silver chloroiodide tabular grains having (111) crystal faces, at least 75 mole % of chloride and up to 3 mole % of iodide, having an average aspect ratio of at least 8:1, an average grain thickness of from 0.08 to less than 0.2 μm and wherein at least 50 % of the total projected area of all the grains is provided by said tabular grains.
- coating said emulsion on at least one side of a support to form a light-sensitive photographic material
- processing said photographic material by the steps of hardener-free developing, hardener-free fixing, rinsing and drying in a total processing time of up to 50 seconds.

## DETAILED DESCRIPTION OF THE INVENTION

To increase the advantages offered by high chloride concentrations in silver halide emulsion crystals rich in chloride it is preferred to limit the presence of other halides so that chloride accounts for at least 75 mole % , and more preferably for at least 95 mole %, based on silver, of the completed emulsion. The inclusion of iodide ions, whether or not in the presence of bromide, in small amounts, has been observed to improve not only the sensitivity but also the tabularity of the emulsions. Preferred tabularities (ratio of aspect ratio and grain thickness expressed in $\mu$m) of at least 40 are highly appreciated as such high values are decisive for the high spectral sensitivity of the emulsion grains. The presence of iodide ions stabilises the (111)-crystal faces, opposite to their presence in crystals having (100)-major faces where the presence of iodide is a "matter of choice" as described in EP-A 0534 395.

Iodide and bromide ions can be incorporated into the grains, rich in chloride, during the nucleation step and/or during the growth step. Although preferred with respect to intrinsic and to spectral sensitivity it is recommended to limit iodide concentrations to up to 3 mole % and even more preferably to limit them to 1.0 mole % or less, based on the total silver amount as higher concentrations retard development and lead to unsatisfactory sensitivities. Moreover the velocity of fixation can be disturbed in that case and as a consequence residual colouration may be unavoidable.

Bromide ion concentrations of up to 25 mole % based on the total silver amounts are contemplated, but in order to avoid a strong inhibition of the processing, the tabular silver chlorobromoiodide emulsion crystals used according to this invention preferably contain an amount of silver bromide of at most 10 mole %. To reduce the amount of replenisher in the processing, it is even more preferable to reduce the amount of bromide ions to less then 5 mole %. Bromide ions can be provided from at least one inorganic and/or organic agent providing bromide ions.

Preferred emulsions comprising silver chlorobromoiodide or chloroiodide tabular crystals used according to this invention are those wherein an amount of 50 to 100 mole % of the total amount of iodide ions is located at the surface of the said emulsion crystals. The presence of iodide ions at the surface of the silver chloroiodide or silver chlorobromoiodide tabular crystals is particularly preferred as upon spectral sensitisation, an improved adsorption of the spectral sensitizer and an improved light absorption is obtained as the quantum efficiency detected in the photochemical processes is increased. Iodide ions are incorporated at the surface of said crystals by means of the so-called conversion technique. Iodide ions can be provided by the addition to the reaction vessel of inorganic iodide salts as e.g. potassium iodide, but for kinetic reasons, especially to obtain a more homogeneous iodide distribution, not only in the crystal lattice but over the whole crystal population, it can be more preferable to add iodide ions provided by organic agents releasing iodide ions or even by a combination of inorganic and organic agents providing iodide ions. Such agents have been described in EP-A 563 701, 563 708 and 561 415 and EP-Applications 93202899.6, filed October 15, 1993, and 93203040.6, filed October 29, 1993. Said agents releasing iodide ions promote a homogenous distribution of iodide ions in the crystal lattice and over the crystal population of the silver chlorobromoiodide or chloroiodide tabular crystals as the precipitation proceeds after homogenisation of the reagents added to the reaction vessel that are slowly releasing iodide ions.

In accordance with this invention it has been found that emulsions comprising tabular grains rich in chloride, having a flat hexagonal shape, are very useful in photographic elements if said grains contain at least 75 mole % of chloride, if at least 50 % of the total projected area of all the grains is provided by said tabular grains, if said tabular grains exhibit an average aspect ratio, defined as the ratio of the average equivalent diameter of the projective tabular crystal surface and its average thickness, of at least 8:1, and if the average thickness is from 0.08 $\mu$m to 0.2 $\mu$m as is illustrated in the Examples given hereinafter. Ultrathin grains with a thickness of less than 0.06 $\mu$m have been given in EP-A 0 534 325

In accordance with this invention it is preferred that at least 70 % of the total projected area is provided by said tabular grains, and even more preferably at least 90 %. In accordance with this invention an aspect ratio of at most 100:1 and more preferably of up to 50:1 is further preferred.

For the preparation of emulsions of tabular silver chloroiodide or silver chlorobromoiodide according to this invention the following preparation steps are included:

a. A nucleation step performed by simultaneously introducing in a dispersion medium in a reaction vessel containing gelatin and adenine a solution providing silver ions and a solution providing chloride, iodide and eventually bromide ions that are added at a constant flow rate during a nucleation time of less than 60 seconds, preferably about 30 seconds, during which an amount of 0.5 % to 5.0 % of the total silver amount is precipitated. Before the start of the precipitation the concentration in the dispersion medium of adenine is established between $10^{-4}$ and $10^{-2}$ molar and is maintained during precipitation between those values. Other compounds that are useful instead of adenine, include substances disclosed in EP-A 481 133 and in EP-A 532 801.

b. A physical ripening step during which the temperature can be varied if necessary and during which additional ingredients as e.g. gelatin, demineralized water etc. are added under stirring. In a preferred mode the precipitation reaction of the tabular silver chlorobromoiodide or chloroiodide emulsion crystals according to this invention proceeds in a dispersing medium wherein the ratio by weight of gelatin to the equivalent amount of silver nitrate is up to 0.35.

c. One or more consecutive double jet growth steps by introducing a solution providing silver ions and a solution providing halide ions, that have the same or a different composition than in the nucleation step, and that are added at a constant or a linearly increasing flow rate to the reaction vessel. The flow rate of the solution providing halide ions can be varied manually or automatically in order to get a constant mV-value, measured as the pAg value by a silver electrode in the reaction vessel. These flow rates can be monitored by e.g. magnetic valves. The different steps of the precipitation can be alternated by physical ripening steps.

It is crucial for the succesful preparation of tabular crystals according to the present invention that before the start and during the different stages of the precipitation the pCl is maintained between 1.0 and 2.0, preferably between 1.0 and 1.5, and pH is maintained between 5.0 and 9.0, preferably between 5.5 and 7.0.

d. Cooling the emulsion mixture to about 40 °C, adding a flocculate like e.g. polystyrene sulphonic acid and adjusting the pH value of the said dispersing medium with an acid to a pH value in order to get a flocculate; decanting said flocculate and washing it with demineralized water in order to remove the soluble salts and the development inhibiting adenin to an allowable residual amount or applying an ultrafiltration washing procedure as disclosed e.g. in Research Disclosure Vol. 102, Oct. 1972, Item 10208, Research Disclosure Vol. 131, March, Item 13122 and Mignot US 4,334,012. Preferably, at the start of the ultrafiltration, pH and pAg are the same as at the end of the precipitation without any adjustment. Preferred values of pH and pAg are chosen in such a way as to optimize the removal of adenin from the emulsion crystal surfaces. As has been established in EP-A 481 133, preferred values of pH are about 4.00 and more preferably about 3.00 whereas preferred values of pAg are about 200 mV and more preferably about 100 mV.

In accordance with this invention it is preferred that tabular silver chlorobromoiodide or chloroiodide emulsion crystals are obtained having an amount of residual adenin of at most 0.3 mg per g of the equivalent amount of silver nitrate which is realized by applying the procedure set forth above. A low amount of residual adenin is in favour of spectral and chemical sensitisation and of the developability of the tabular crystals in the processing. Adenine is well-known as a habit modifying agent in the preparation of tabular crystals rich in chloride having (111) major faces as has been shown in EP-A 0 481 133.

In the preparation of tabular crystals according to the present invention there is no need for the use of a special oxidized gelatin or the presence of a synthetic peptizer. 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 enzyme-treated as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966).

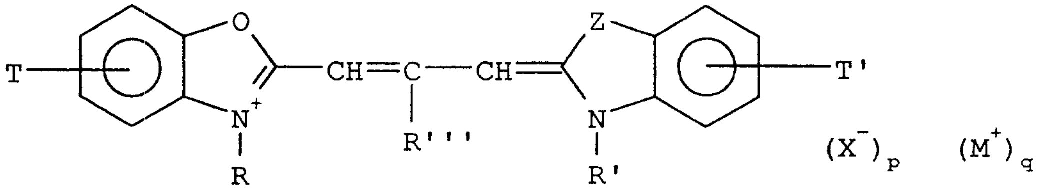
Additional gelatin can be added at a later stage of the emulsion preparation, e.g. after washing, to establish optimal coating conditions and/or to establish the required thickness of the coated emulsion layer. Preferably a gelatin to silver halide ratio, the silver halide being expressed as the equivalent amount of silver nitrate, ranging from 0.3 to 1.0 is then obtained.

In classical emulsion preparation spectral sensitisation traditionally follows the completion of chemical sensitisation. However in connection with tabular grains according to this invention, it is highly contemplated that spectral sensitisation can occur simultaneously with or even precede completely the chemical sensitisation step.

So it can be advantageous to add an amount of a spectral sensitising dye to the emulsion crystals just before cooling of the dispersion at the end of the growth stage, but in principle the addition of said dye may be performed at any stage of the precipitation, during or after redispersing or before, during or after chemical ripening. The addition can further be performed in one or more portions.

It is preferred that the tabular silver chlorobromoiodide or chloroiodide emulsion crystals are spectrally sensitised with at least one spectral sensitiser having a J-aggregating structure when adsorbed at the crystal surface of the tabular grains according to this invention.

In a preferred embodiment tabular silver chlorobromoiodide or chloroiodide emulsion crystals according to this invention are spectrally sensitised with at least one dye having a structure corresponding to the general formula (I) given below.



(I)

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' may each independently represent the usual substituents known in the art,
$(X^-)_p$ represents an 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, wherein p and q each represent an integer in order to get an electronically neutral compound.
Preferred spectral sensitisers suitable for use together with the emulsion crystals according to this invention are those of the type where R''' is $-C_2H_5$, Z is an oxygen atom, at least one of R and R' represents

- a sulphoalkyl group, preferably corresponding to the formulae
  $-(CH_2)_nSO_3^-$ wherein n equals 2, 3 or 4,
  $-(CH_2)_2-CH(CH_3)-SO_3^-$
  and $-CH_2-CHY-CH_2-SO_3^-$ wherein Y represents -OH or -Cl;
- a sulphatoalkyl group, preferably corresponding to the formula
  $-(CH_2)_nOSO_3^-$ wherein n equals 2, 3 or 4,
- an acylsulphonamido group, preferably corresponding to the formulae
  $-(CH_2)_n-C(O)-N($R''''$)-SO_2-(CH_2)_mH$ wherein n equals 1, 2 or 3; m equals 1, 2, 3, etc.
  $-(CH_2)_r-SO_2-N($R''''$)-SO_2-(CH_2)_sH$ wherein r equals 2, 3 or 4; s equals 1, 2, 3, etc.,
  $-(CH_2)_v-SO_2-N($R''''$)-C(O)-(CH_2)_wH$ 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 independantly represent 5-phenyl, 5-Cl, 5-$OCH_3$ and 5-$CH_3$.

Another class of preferred spectral sensitisers suitable for use together with the emulsion crystals according to this invention are those of the type where R''' is hydrogen, Z is an nitrogen atom, wherein T represents 5-phenyl, 5-Cl, 5-$OCH_3$ and 5-$CH_3$ and wherein T' represents 5,6-$(Cl)_2$; 5-CN-6-Cl; 5-$CF_3$-6-Cl; 5-Cl; 5-CN, 5-$CF_3$, 5-$CHF_2$, 5-$SO_2CH_3$, 5-$SO_2$R''''' (R''''' representing a fluoro-subsituted or non-fluoro-substituted alkylgroup), 5-COOR'''''' and 5-$SO_2$-N($R^x$) ($R^y$) or 5-CO-N($R^x$) ($R^y$), wherein $R^x$ and $R^y$ each independently represent substituted or unsubstited alkyl groups, which may 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' represent all combinations of the formulae
$-(CH_2)_nSO_3^-$ wherein n equals 2, 3 or 4,
$-(CH_2)_2-CH(CH_3)-SO_3^-$
and $-CH_2-CHY-CH_2-SO_3^-$ wherein Y represents -OH or -Cl; and wherein R, corresponding to the formulae given above, is combined with R' corresponding to the formulae
$-(CH_2)_jH$ wherein j equals 1, 2, 3 or 4;
$-CH_2$-Phen-$SO_3^-$
$-CH_2$-Phen-COOH
$-(CH_2)_k$-Phen-COOH wherein k equals 1, 2 or 3.

An example of a useful spectral sensitiser according to the general formula given above is anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyloxacarbo-cyanine hydroxide or anhydro-5,5'-dichloro-3,3'-bis(n-sulphopropyl)-9-ethyloxacarbocyaninehydroxide.

A suitable mixture of spectral sensitizers that is applied is anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyl oxacarbocyanine hydroxide or anhydro-5,5'-dichloro-3,3'-bis(n-sulphopropyl)-9-ethyloxacarbocyanine hydroxide together with anhydro-5,5'-dicyano-1,1'-diethyl-3,3'-di(2-acetoxyethyl)-ethylimidacarbocyanine bromide.

Two or more types of tabular silver halide emulsions that have been prepared differently can be mixed for forming a photographic emulsion for use in accordance with the present invention.

The size distribution of the grains in the emulsions comprising the silver chlorobromoiodide or chloroiodide tabular grains according to the present invention can be monodisperse or heterodisperse, the monodisperse distribution being preferred.

The emulsion comprising the silver halide tabular grains in connection with the present invention can be chemically sensitised as described e.g. in "Chimie et Physique Photographique" by P. Glafkides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in the literature mentioned above chemical sensitisation can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines as well as in the corresponding selenium derivatives. 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 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds.

The silver halide emulsion layer(s) in accordance with the present invention or the non-light-sensitive layers may comprise compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of the photographic elements or during the photographic treatment thereof. Many known compounds can be added as fog-inhibiting agent or stabilizer to the silver halide emulsion layer or to other coating layers in water-permeable relationship therewith such as an undercoat or a topcoat protective layer. Suitable examples are e.g. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JA-Appl. 75-39537, and GB 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide as well as the compounds described in Research Disclosure N° 17643 (1978), Chapter VI. Many of these fog-inhibiting compounds may have been already added before or during the chemical ripening of the tabular silver halide crystals.

The photographic tabular grains in connection with the present invention can be used in various types of photographic elements. Because of their content rich in chloride such crystals are normally used for those applications which do not require extreme high sensitivity as in graphic arts e.g. recording materials for the output of scanners, phototypesetters and imagesetters, duplicating materials, radiographic hard-copy materials, diffusion transfer materials and black-and-white or colour print materials which produce prints starting from negatives in amateur or professional still photography or prints for cinematographic exhibition.

It has now been found unexpectedly that due to the presence of iodide ions in said grains rich in chloride according to this invention sensitivities can be attained which have hitherto never been reached with such spectrally sensitised grains. Especially the combination of the specific iodide profile, preferably at the surface of the grains rich in chloride, together with the high tabularity makes them, for the first time, particularly useful also for applications which require higher sensitivities as e.g. X-ray photographic materials for medical diagnosis and colour negative materials.

The photographic material according to this invention comprises a support and on at least one side thereof at least one silver halide light-sensitive emulsion layer comprising silver chlorobromoiodide and/or chloroiodide tabular crystals as described hereinbefore.

Development acceleration can be accomplished by incorporating in the emulsion layer or adjacent layers various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US Patents 3,038,805; 4,038,075 and 4,292,400 as well as in EP-A 634 688 and 94200639, filed March 11, 1994.

The photographic element of the present invention may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulpho, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g higher contrast, sensitization, and development acceleration. Preferred surface-active coating agents are compounds containing perfluorinated alkyl groups.

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 and plasticizers.

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

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

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

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, GB Patent 7,907,440, EP-A's 0 586 748 and 0 587 230, US-P 5,344,749 and EP-A No. 93203382.2, filed December 2, 1993.

Coated 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 resulting in shorter drying times after washing in the processing cycle.

The gelatin binder of the photographic material according to this invention 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. 1,3-vinylsulphonyl-2-propanol, di-(vinyl-sulphonyl)-methane or ethylene di-(vinyl-sulphone), chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methyloldimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binder can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US-P 4,063,952 and with the onium compounds as disclosed in EP-A 408,143.

The photographic material according to this invention is preferably hardened to such an extent that the total amount of water absorption is at most 10 g/m$^2$ per side after immersing the material for 3 minutes in demineralized water of 25 ° C.

The photographic element according to this invention can 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 the invention. By using duplitized emulsions differing in photographic speed by at least 0.15 log E a gain in cross-over exposure in double side coated materials can be obtained. Besides the light sensitive emulsion layer(s) the photographic material may contain several light-insensitive layers, e.g. a protective layer, one or more backing layers, one or more subbing layers, one or more intermediate layers e.g. filter layers and even an afterlayer containing e.g. the hardening agent(s), the antistatic agent(s), filter dyes for safety-light purposes etc.

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.

In a preferred embodiment the photographic material according to this invention is a double side coated X-ray material with a cross-over percentage of less than 40% even in the absence of an antihalation undercoating. The cross-over percentage (% cross-over) is therein determined as follows. The double side coated materials are adjusted between a single green light emitting screen (CURIX ortho Regular : Agfa-Gevaert trade name) and a white paper, replacing the second screen. This film-screen element, directed with its light emitting screen to the X-ray tube, is then exposed with varying X-ray doses, expressed as log E. After processing these samples in the 90 seconds cycle specified further in the Examples, the minimal dose (log E) needed to obtain a density of 0.5 above fog is determined for the frontlayer (log E front) and the backlayer (log E back) separately. The cross-over percentage is then calculated according to the following equation :

$$\%\ \text{cross-over} = 100/\text{antilog}(\log E\ \text{back} - \log E\ \text{front})$$

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 containing tabular 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 tabular 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. Applications within total processing times of 30 seconds and lower up to 90 seconds, known as common praxis, are possible.

According to this invention processing of a photographic material comprising the steps of developing, fixing, rinsing and drying can proceed, with a total processing time of at most 45 seconds thanks to the high degree of hardening of the said material as set forth hereinbefore. More preferably a processing of at most 38 seconds is possible.

Further according to this invention processing proceeds in a hardener-free developer and/or fixer. In a preferred embodiment the developing proceeds in a developer comprising ascorbic acid as a developing solution.

From an ecological point of view it is a preferred embodiment to use sodium thiosulphate instead of ammonium thiosulphate in the fixer the fixation thus proceeding ammonium-free. In these particular conditions processing according to this invention proceeds with reduced amounts for the regeneration of the developing and fixing solutions, the said amounts corresponding to at most 200 ml/m$^2$ and 300 ml/m$^2$ respectively.

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

EXAMPLES

Emulsion A (tabular silver chloride emulsion)

The following solutions were prepared :

- 3 l of a dispersion medium (C) containing 0.444 moles of sodium chloride, 15 g of inert gelatin and 270 mg of adenine; temperature was established at 45 °C and pH was adjusted to 5.5;
- a 2.94 molar silver nitrate solution (A);
- a solution containing 4.476 moles of sodium chloride and 420 mg of adenin (B1);

A nucleation step was performed by introducing solution A and solution B1 simultaneously in dispersion medium C both at a flow rate of 30 ml/min during 30 seconds. After a physical ripening time of 15 min during which the temperature was raised to 70 °C and 97.5 g of gelatin and 1500 ml of water were added and the mixture was stirred for an additional 5 minutes. Then a growth step was performed by introducing by a double jet during 66 minutes solution A starting at a flow rate of 7.5 ml/min and linearly increasing the flow rate to an end value of 37.5 ml/min, and solution B1 at an increasing flow rate as to maintain a constant mV-value, measured by a silver electrode versus a saturated calomel electrode (S.C.E.), of +92 mV.

To this dispersion medium an amount of 1.25 mmole per mole of silver chloride was added of the dye anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyloxacarbo-cyanine hydroxide.

After cooling to about 40 °C the pH value of the said dispersing medium was adjusted to a value of 3.0 with sulphuric acid, and after the addition of 55.5 ml of polystyrene sulphonic acid the obtained flocculate was decanted and washed three times with an amount of 6 l of demineralized water in order to remove the soluble salts present.

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

Emulsions B1 to B6 (comparative tabular silver chloroiodide emulsions)

For the preparation of the Emulsions B1 to B6, an amount of potassium iodide was added to B1, in order to obtain an iodide content in the tabular silver chloroiodide crystals of respectively 0.25 (B1); 0.50 (B2); 0.75 (B3); 1.00 (B4); 1.50 (B5) and 2.00 (B6) mole %. Grain characteristics are summarized in Table 1.

Table 1

| Emulsion | $d_{EM}$ (µm) | d (µm) | AR | $d_M$ (µm) |
|---|---|---|---|---|
| A (comp. AgCl) | 1.20 | 0.37 | 3.3 | 0.66 |
| B1 (comp. AgCl(I)) | 1.22 | 0.38 | 3.2 | 0.48 |
| B2 (comp. AgCl(I)) | 1.11 | 0.38 | 3.0 | 0.44 |
| B3 (comp. AgCl(I)) | 1.18 | 0.34 | 3.5 | 0.62 |
| B4 (comp. AgCl(I)) | 1.21 | 0.33 | 3.6 | 0.54 |
| B5 (comp. AgCl(I)) | 1.15 | 0.34 | 3.3 | 0.54 |
| B6 (comp. AgCl(I)) | --- | --- | <3.0 | 0.36 |

From Table 1 it can be concluded that it is difficult to controll the growth of such tabular crystals in order to get reproducible and predictable grain sizes as there is no detectable trend in these data as a function of iodide content of the corresponding tabular silver chloride crystals. Moreover the average aspect ratio is rather low (even less than 5) and the thickness of the crystals rather high (at least 0.3 µm).

Before the start of the chemical ripening the mV-value of every emulsion was adjusted at +120 mV with sodium chloride and the pH-value at 5.5 with sodium hydroxide. Chemical ripening agents were adapted to the crystal size of the emulsions.

Chemical ripening agents were gold thiocyanate, sodium thiosulphate as a source of sulphur and toluene thiosulphonic acid was used as predigestion agent. The amounts of each chemical ripening were optimized in order to obtain an optimal fog-sensitivity relationship after 2 hours at 57 °C.

Before coating each emulsion was stabilized with 1-p-carboxyphenyl-5-mercaptotetrazole and after addition of the normal coating additives the solutions were coated simultaneously together with a protective layer containing 1.3 g gelatine per $m^2$ per side on both sides of a polyethylene terephthalate film support having a thickness of 175 µm. The resulting photographic material contained per side an amount of silver halide corresponding to 4.5 grams of $AgNO_3$ per $m^2$ and an amount of gelatin corresponding to 3.55 $g/m^2$.

The absorption spectra measured from the unexposed and unprocessed materials show an increase of the absorption density at a wavelength value of 510 nm and of 545 nm with respectively about 20 and 80 %, corresponding to the absorption maxima of the spectrally sensitizing dye adsorbed at the silver chloride crystal surface and in the gelatin matrix. From these data it can be concluded that the tabular silver chloride crystals containing iodide ions show an improved dye absorption if compared with tabular silver chloride crystals prepared iodide-free (see Fig. 1: absorption curve for iodide-free silver chloride crystals; Fig. 2: absorption curve for silver chloride crystals having a silver iodide containing phase at its crystal surface).

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 "90 seconds cycle" described below. The processing occurred in a glutaraldehyde containing hydroquinone/1-phenyl-3-pyrazolidinone developer marketed by Agfa-Gevaert N.Y. under the trade name G138 having a high activity. The processing occurred in the processing machine CURIX 402 (Agfa-Gevaert trade name) with the following time (in seconds (sec.)) and temperature (in °C) characteristics:

| | |
|---|---|
| loading | 3.4 sec. |
| developing | 23.4 sec./ 35 °C high or low activity developer |
| cross-over | 3.8 sec. |
| fixing | 15.7 sec./ 35 °C in fixer AGFA G334 (trade name) |
| cross-over | 3.8 sec. |
| rinsing | 15.7 sec./ 20 °C. |
| drying | 32.2 sec. (cross-over time included) |
| total time: | 98.0 sec. |

It was however not possible to obtain the required sensitometric specifications as obtained with the normally used silver bromide or silver bromoiodide emulsions in comparison with all those emulsions: insufficient densities were obtained and the average speed value should be enhanced with a factor of about 2.

Even in a processing composition more suitable for the development of silver halide crystals rich in chloride, no satisfying results could be obtained. Said processing composition is given hereinafter:

| | |
|---|---|
| demineralized water | 500 ml |
| hydroquinone | 40 g |
| phenidone B | 1.6 g |
| potassium bromide | 5 g |
| potassium thiocyanate | 2 g |
| aqueous potassium sulphite (655 g/l) | 300 ml |
| aqueous potassium carbonate (765 g/l) | 80 ml |
| aqueous potassium hydroxyde (755 g/l) | 14 ml |
| Trilon B (trade name for $Na_4$EDTA from BASF) | 8 ml |
| Turpinal 2NZ (trade name for 1-hydroxy-ethyldiphosphonic acid disodium salt) | 2 g |
| Polyoxyethylene (M.W.: 200) | 40 ml |
| pH | 10.70 |
| Water to make 1 l | |

The concentrated, hardener-free developer, called "CHLORDEV" has to be diluted with the same amount of demineralised water (pH of developer ready-for-use: 10.46). In Table 2 the sensitometric results obtained are given.

Samples of these coatings had been exposed with green light of 540 nm during 0.1 seconds using a continuous wedge and had been processed during the 98 seconds cycle described hereinbefore.

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 relative speed S at a density of 1 above fog (an increase of the said speed with a factor of 2 gives a speed value that is 0.30 lower as the relation is logarithmic and as less light is needed to get the desired density),
- the contrast expressed as gradation G, calculated between the densities 0.25 and 2.0 above fog,
- the maximum density DMAX

Table 2

| Emulsion | F | S | G | DMAX |
|---|---|---|---|---|
| A (comp. AgCl) | 0.037 | 2.65 | 2.77 | 2.79 |
| B1 (comp. AgCl(I)) | 0.040 | 2.00 | 2.13 | 3.01 |
| B2 (comp. AgCl(I)) | 0.041 | 2.01 | 2.24 | 3.11 |
| B3 (comp. AgCl(I)) | 0.050 | 1.97 | 1.97 | 3.31 |
| B4 (comp. AgCl(I)) | 0.044 | 2.01 | 2.42 | 3.29 |
| B5 (comp. AgCl(I)) | 0.045 | 2.32 | 2.32 | 3.09 |
| B6 (comp. AgCl(I)) | 0.020 | 2.71 | 2.71 | 2.26 |

From Table 2 it can be concluded that the presence of iodide ions is required for sensitivity. Otherwise the presence of tabular grains having an aspect ratio that is too low makes it difficult to reach the desired sensitometric specifications.

Emulsions K1-K2 (comparative tabular silver chlorobromide emulsion)

The said emulsions K1 and K2 were prepared without the presence of iodide ions, nor in B1, nor in B2. Instead of potassium iodide potassium bromide was added to B1 in an amount in order to obtain a silver chlorobromide emulsion having 5 mole % of bromide for K1 and 10 mole % of bromide for K2.

Therefor the following solutions were prepared :

- 3 l of a dispersion medium (C) containing 0.330 moles of sodium chloride, 75 g of inert gelatin and 180 mg of adenine; temperature was established at 45 °C and pH was adjusted to 5.5; a value of 91 mV versus S.C.E. was measured by a silver electrode.
- a 2.94 molar silver nitrate solution (A);
- 1 l of a solution containing 2.968 moles of sodium chloride, 280 mg of adenin (B1) and potassium bromide in an amount of 5 (K1), resp. 10 (K2) mole %.

A nucleation step was performed by introducing solution A and solution B simultaneously in dispersion medium C both at a flow rate of 60 ml/min during 30 seconds. After a physical ripening time of 20 min during which the temperature is raised to 70 °C a growth step was performed by introducing by a double jet during 28 minutes and 48 seconds solution A starting at a flow rate of 5 ml/min and linearly increasing the flow rate to an end value of 13.73 ml/min, and solution B at an increasing flow rate in order to maintain a constant mV value, measured by a silver electrode versus S.C.E., of +103 mV. The said growth step was continued at a the lower starting flow rate for solution A of 5 ml/min during 16 minutes while solution B was added at a flow rate so as to maintain the mV at a constant value of +135 mV. A further increase to a flow rate of 25 ml/min. in a time period of 41 minutes and 20 seconds for solution A was the next step, during which the pAg value was kept at +135 mV.

After cooling to about 40 °C 23 ml of polystyrene sulphonic acid was added and the pH value of the said dispersing medium was adjusted to a value of 3.0 with sulphuric acid. The flocculate obtained was decanted and washed three times with an amount of 4 l of demineralized water in order to remove the soluble salts present.

Values of $d_M$ (in $\mu$m) were determined as described hereinbefore: values of 0.79 and 0.81 were measured for emulsions K1 and K2 resp..

Emulsions L1-L2 (comparative tabular silver chlorobromoiodide emulsions)

Same solutions and procedure as for K1 and K2, except for the addition at the end of the growth step of a B2 solution of potassium iodide in order to get silver chorobromoiodide crystals having an iodide content of 0.8 mole % (B2 was added at a flow rate of 20 ml/min after a physical ripening time of 1 minute).

Values of $d_M$ (in $\mu$m) were determined as described hereinbefore: values of 0.79 and 0.81 were measured for emulsions L1 and L2 resp..

The emulsions K1, K2, L1 and L2 were coated in the same way as described hereinbefore for the emulsions A and B1-B6.

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 90 seconds cycle described before.
The processing occurred in a developer containing glutaraldehyde as a hardener and hydroquinone/1-phenyl-3-pyrazolidinone as main developing agents, marketed by Agfa-Gevaert N.V. under the tradename G138 having a high activity and in the above described hardener-free developer "CHLORDEV".

The density as a function of the light dose was measured and therefrom were determined the sensitometric parameters as described hereinbefore (see also Table 2). Results obtained for fog F, sensitivity S, contrast G and maximum density DMAX with the said emulsions are summarized in Table 3.

Table 3

| Emulsion/ Dev. | F | S | G | DMAX |
|---|---|---|---|---|
| K1/G138 | 0.057 | - | - | 1.00 |
| K1/CHLORDEV | 0.114 | 2.78 | - | 2.09 |
| L1/G138 | 0.074 | 2.16 | 2.09 | 2.60 |
| L1/CHLORDEV | 0.066 | 2.09 | 2.18 | 2.73 |
| K2/G138 | 0.208 | - | - | 1.16 |
| K2/CHLORDEV | 0.117 | 2.89 | - | 1.58 |
| L2/G138 | 0.212 | 2.34 | - | 2.16 |
| L2/CHLORDEV | 0.156 | 2.19 | 1.80 | 2.48 |

From the data given in Table 3 it can be concluded that the incorporation of bromide ions into the crystal lattice promotes, although insufficiently, the absorption by the emulsion crystals coated of light with a wavelength corresponding to the one emitted by the intensifying screens. The addition of iodide ions at the end of the preparation step, although required to give the desired J-aggregation of the dye at the crystal surface, doesn't give rise to convincing results. Moreover the low aspect ratios of the tabular silver chlorobromoiodide crystals are satisfying neither.

Emulsions T1-T8 (inventive tabular silver chloroiodide emulsions)

For the preparation of the Emulsions T1-T8, an amount of potassium iodide was added to B1, just as for the comparative Emulsions B1-B6 in order to obtain an iodide content in the tabular silver chloroiodide crystals of 1.3 mole %. Variable parameters in the preparation method of the inventive Emulsions T1-T8 were the concentration of adenin in the reaction vessel (given in mg per 500 g of silver nitrate used in the precipitation, the pAg value (expressed in mV vs. S.C.E.) during the nucleation step and the temperature T (in °C) of the reaction vessel in the said nucleation step. The values of the said parameters are summarized in Table 4, as well as the tabular grain characteristics, the data given herein corresponding with those given in Table 1.

Table 4

| Em. | $d_{EM}$ (µm) | d (µm) | AR | $d_M$ (µm) | [adenin] | pAg | T |
|---|---|---|---|---|---|---|---|
| T1 | 1.27 | 0.14 | 8.8 | 0.70 | 460 | + 91.0 | 45 |
| T2 | 2.70 | 0.16 | 16.5 | 1.22 | 460 | +107.5 | 45 |
| T3 | 1.70 | 0.14 | 12.3 | 0.84 | 460 | + 96.0 | 70 |
| T4 | 1.77 | 0.08 | 22.0 | 0.72 | 920 | +107.5 | 45 |
| T5 | 2.27 | 0.14 | 16.6 | 1.02 | 920 | +126.5 | 45 |
| T6 | 1.48 | 0.09 | 17.0 | 0.66 | 920 | + 96.5 | 70 |
| T7 | 2.08 | 0.12 | 18.0 | 0.91 | 920 | +114.5 | 70 |
| T8 | 2.21 | 0.10 | 22.0 | 0.91 | 920 | +135.0 | 70 |

The Emulsions T1-T8 were chemically and spectrally sensitised and further coated in the same way as described hereinbefore for the Emulsions J, K and L.

The coatings were exposed in the same way and the processing which was performed as in the G138 developer from Agfa-Gevaert containing hardening agent and in the experimental hardener-free developer CHLORDEV replacing G138, the composition of which is given above.

Data for the temperature (TNUC) and for the UAg-value (UAG) (in mV vs. a Ag/AgCl reference electrode) during the nucleation step are given in Table 5.

Results obtained for fog F, sensitivity S, contrast G and maximum density DMAX with emulsions T1-T8 are summarized in Table 5, just as in Table 3. The specifications for a CURIX ORTHO film material, trade name product from Agfa-Gevaert, which have to be attained, are added to the Table 5.

Table 5

| Emulsion/Dev. | F | S | G | DMAX | TNUC (°C) | UAG (mV) |
|---|---|---|---|---|---|---|
| T1/G138 | 0.044 | 1.78 | 2.86 | 3.35 | 45 | 91 |
| T1/CHLORDEV | 0.049 | 1.69 | 3.16 | 3.01 | 45 | 91 |
| T2/G138 | 0.069 | 1.74 | 3.46 | 2.82 | 45 | 107.5 |
| T2/CHLORDEV | 0.104 | 1.69 | 2.44 | 2.47 | 45 | 107.5 |
| T3/G138 | 0.061 | 1.87 | 3.09 | 2.94 | 70 | 96.5 |
| T3/CHLORDEV | 0.087 | 1.81 | 2.94 | 2.67 | 70 | 96.5 |
| T4/G138 | 0.049 | 1.82 | 3.63 | 4.10 | 45 | 107.5 |
| T4/CHLORDEV | 0.067 | 1.67 | 4.15 | 3.87 | 45 | 107.5 |
| T5/G138 | 0.051 | 1.96 | 2.36 | 3.23 | 45 | 126.5 |
| T5/CHLORDEV | 0.056 | 1.80 | 2.89 | 3.10 | 45 | 126.5 |
| T6/G138 | 0.047 | 1.87 | 3.26 | 3.63 | 70 | 96.5 |
| T6/CHLORDEV | 0.082 | 1.73 | 3.63 | 3.51 | 70 | 96.5 |
| T7/G138 | 0.055 | 1.84 | 3.40 | 3.63 | 70 | 114.5 |
| T7/CHLORDEV | 0.094 | 1.71 | 3.50 | 3.13 | 70 | 114.5 |
| T8/G138 | 0.070 | 1.65 | 3.37 | 3.53 | 70 | 135 |
| T8/CHLORDEV | 0.081 | 1.63 | 3.28 | 2.98 | 70 | 135 |
| CURIX ORTHO | 0.030 | 1.67 | 2.87 | 3.51 | | |

From the data given in Table 5 it can be concluded that silver halide photographic materials containing the silver chloroiodide tabular crystals T1-T8, according to this invention, are useful as the required sensitometric specifications are attained.

Moreover the differences between the sensitometries obtained after processing the materials in G138 and in CHLORDEV are reduced if compared with the results obtained in Table 3. In other words: the developing capacity is increased to an unexpected extend.

Further a comparison was made between the sensitometric data obtained in G138-chemistry (90 seconds processing time) and in a 38 seconds processing cycle in the 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 "CHLORAP" described below |
| cross-over | 1.4 sec. |
| rinsing | 0.9 sec. |
| cross-over | 1.5 sec. |
| fixing | 6.6 sec. 35°C in fixer "CHLORAP" 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 Developer "CHLORAP":

| -concentrated part : | |
|---|---|
| water | 200 ml |
| potassium bromide | 12 grams |
| potassium sulphite (65% solution) | 249 grams |
| ethylenediaminetetraacetic acid, 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 |
| potassium iodide | 0.022 grams |
| 4-hydroxymethyl-4methyl-1phenyl-3-pyrazolidinone | 3 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 Fixer "CHLORAP":

| -concentrated part : | |
|---|---|
| ammonium thiosulfate (78% solution) | 661 grams |
| sodium sulphite | 54 grams |
| boric acid | 25 grams |
| sodium acetate-trihydrate | 70 grams |
| acetic acid | 40 grams |
| water to make 1 liter | |
| pH adjusted with acetic acid to 5.30 at 25 ° C | |

To make this fixer ready-for-use one part of this concentrated part was mixed with 4 parts of water. A pH of 5.25 was measured at 25 ° C.

Data were collected in Table 6 as given hereinbefore for the emulsions T2-T8 after preservation of the materials for 3 days at 57 ° C and 34 % RH.

From the data given in Table 6 it can concluded that quite similar results can be obtained in the hardener-containing, 90 seconds processing cycle and in the hardener-free, 38 seconds processing cycle.

Table 6

| Emulsion/Dev. | F | S | G | DMAX | TNUC ( ° C) | UAG (mV) |
|---|---|---|---|---|---|---|
| T2/G138 | 0.134 | 1.75 | 3.08 | 2.86 | 45 | 107.5 |
| T2/CHLORAP | 0.113 | 1.74 | 2.88 | 2.73 | 45 | 107.5 |
| T3/G138 | 0.098 | 1.94 | 2.66 | 3.00 | 70 | 96.5 |
| T3/CHLORAP | 0.095 | 1.92 | 2.81 | 2.90 | 70 | 96.5 |
| T4/G138 | 0.092 | 1.89 | 2.88 | 4.09 | 45 | 107.5 |
| T4/CHLORAP | 0.107 | 1.89 | 3.14 | 4.08 | 45 | 107.5 |
| T5/G138 | 0.080 | 1.93 | 2.34 | 3.27 | 45 | 126.5 |
| T5/CHLORAP | 0.086 | 2.00 | 2.03 | 3.06 | 45 | 126.5 |
| T6/G138 | 0.103 | 1.93 | 2.83 | 3.70 | 70 | 96.5 |
| T6/CHLORAP | 0.084 | 1.94 | 3.00 | 3.60 | 70 | 96.5 |
| T7/G138 | 0.106 | 1.86 | 2.86 | 3.55 | 70 | 114.5 |
| T7/CHLORAP | 0.105 | 1.90 | 3.07 | 3.07 | 70 | 114.5 |
| T8/G138 | 0.157 | 1.70 | 2.67 | 3.46 | 70 | 135 |
| T8/CHLORAP | 0.123 | 1.70 | 2.94 | 3.50 | 70 | 135 |
| CURIX ORTHO | 0.030 | 1.67 | 2.87 | 3.51 | | |

Emulsions TV1-TV3 (inventive tabular silver chloroiodide emulsions with a variable iodide profile)

For the preparation of the Emulsions TV1-TV3 an amount of potassium iodide was added to B1, and the preparation followed the steps just as for the inventive Emulsions T1-T8 with the difference that the amount of iodide was varied: 0.5 mole % for TV1; 1.0 mole % for TV2 and 2 mole % for TV3. For Emulsions TV2 and TV3 no further additions of iodide were performed, so that the total amount of iodide ions for both Emulsions was 1 mole % and 2 mole % respectively. For Emulsion TV1 an iodide content in the silver chloroiodide tabular crystals of 1.3 mole % was obtained by adding a further amount of 0.8 mole % at the end of the preparation stage just as for the Emulsions L1 and L2. The values of the tabular grain characteristics are summarized in Table 7. The parameters summarised herein correspond to those given in Table 1.

Table 7

| Em. | $d_{EM}$ ($\mu$m) | d ($\mu$m) | AR | $d_M$ ($\mu$m) |
|---|---|---|---|---|
| TV1 | 1.27 | 0.14 | 8.8 | 0.70 |
| TV2 | 1.51 | 0.19 | 8.1 | 0.86 |
| TV3 | 1.25 | 0.17 | 7.5 | 0.73 |

The Emulsions TV1-TV3 were coated in the same way as described hereinbefore for the Emulsions J, K, L and T. The coatings were exposed in the same way as well as the processing which was performed as in the developer G138, from Agfa-Gevaert, containing a hardener and in the hardener-free developer CHLORDEV replacing G138, the composition of which has been given hereinbefore.

Results obtained for fog F, sensitivity S, contrast G and maximum density DMAX with the said emulsions are summarized in Table 7, just as in Tables 3 and 5. The specifications, which should be attained for a CURIX ORTHO film material, trade name from Agfa-Gevaert, processed in G138, are added to this Table.

Table 8

| Emulsion/Dev. | F | S | G | DMAX |
|---|---|---|---|---|
| TV1/G138 | 0.044 | 1.78 | 2.86 | 3.35 |
| TV1/CHLORDEV | 0.049 | 1.69 | 3.16 | 3.01 |
| TV2/G138 | 0.149 | 1.84 | 2.25 | 3.16 |
| TV2/CHLORDEV | 0.143 | 1.68 | 2.30 | 3.02 |
| TV3/G138 | 0.034 | 2.06 | 1.25 | 2.22 |
| TV2/CHLORDEV | 0.070 | 1.71 | 2.21 | 3.20 |
| CURIX ORTHO | 0.030 | 1.67 | 2.87 | 3.51 |

The most favourable relationship between fog, sensitivity and gradation is obtained with the Emulsion TV1: lower amounts of iodide are leading to fog increase, loss in sensitivity and gradation; higher amounts although preventing fog increase are leading to a still more remarkable loss in sensitivity and gradation. The addition of iodide ions at the crystal surface of the silver chlorobromoiodide or silver chloroiodide crystals is thus particularly favourable. Moreover for all samples of the materials coated from emulsions according to this invention a suitable black image tone is observed.

## Claims

1. Emulsion comprising silver chlorobromoiodide or silver chloroiodide tabular grains having (111) crystal faces, having at least 75 mole % of chloride and up to 3 mole % of iodide, having an average aspect ratio of at least 8:1 and an average grain thickness of from 0.08 $\mu$m to less than 0.2 $\mu$m and wherein at least 50 % of the total projected area of all the grains is provided by said tabular grains.

2. Emulsion according to claim 1, wherein at least 70 % of the total projected area of all the grains is provided by said tabular grains.

3. Emulsion according to claim 1 or 2 wherein tabular grains have at most 1 mole % of iodide.

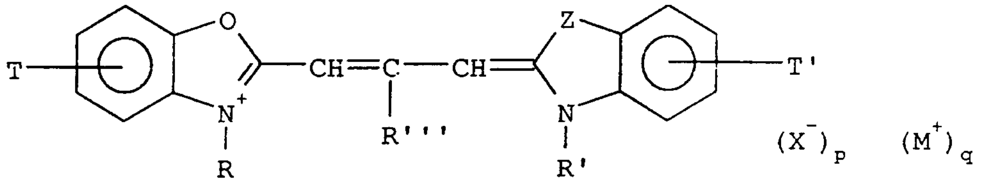
**4.** Emulsion according to any of claims 1 to 3, wherein the tabular grains have an average aspect ratio of at most 50:1.

**5.** Emulsion according to any of claims 1 to 4, wherein an amount of adenin of at most 0.3 mg per g of the equivalent amount of silver nitrate is present.

**6.** Emulsion according to any of claims 1 to 5, wherein said tabular grains have iodide ions at the crystal surface.

**7.** Emulsion according to any of claims 1 to 6, wherein said tabular grains have been spectrally sensitised with at least one spectral sensitizer having a J-aggregating structure.

**8.** Emulsion according to claim 7, wherein the said spectral sensitiser has a structure corresponding to the general formula (I)



(I)

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

**9.** Emulsion according to claim 7 or 8, wherein the said spectral sensitizer is anhydro-5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyloxacarbo-cyanine hydroxide or anhydro-5,5'-dichloro-3,3'-bis(n-sulphopropyl)-9-ethyloxacarbo-cyanine hydroxide.

**10.** Emulsion according to claim 9 wherein said spectral sensitizer is applied in combination with anhydro-5,5'-dicyano-3,3'-bis(N-acetoxyethyl)-1,1'-ethylbenzimidazolcarbocyanine.

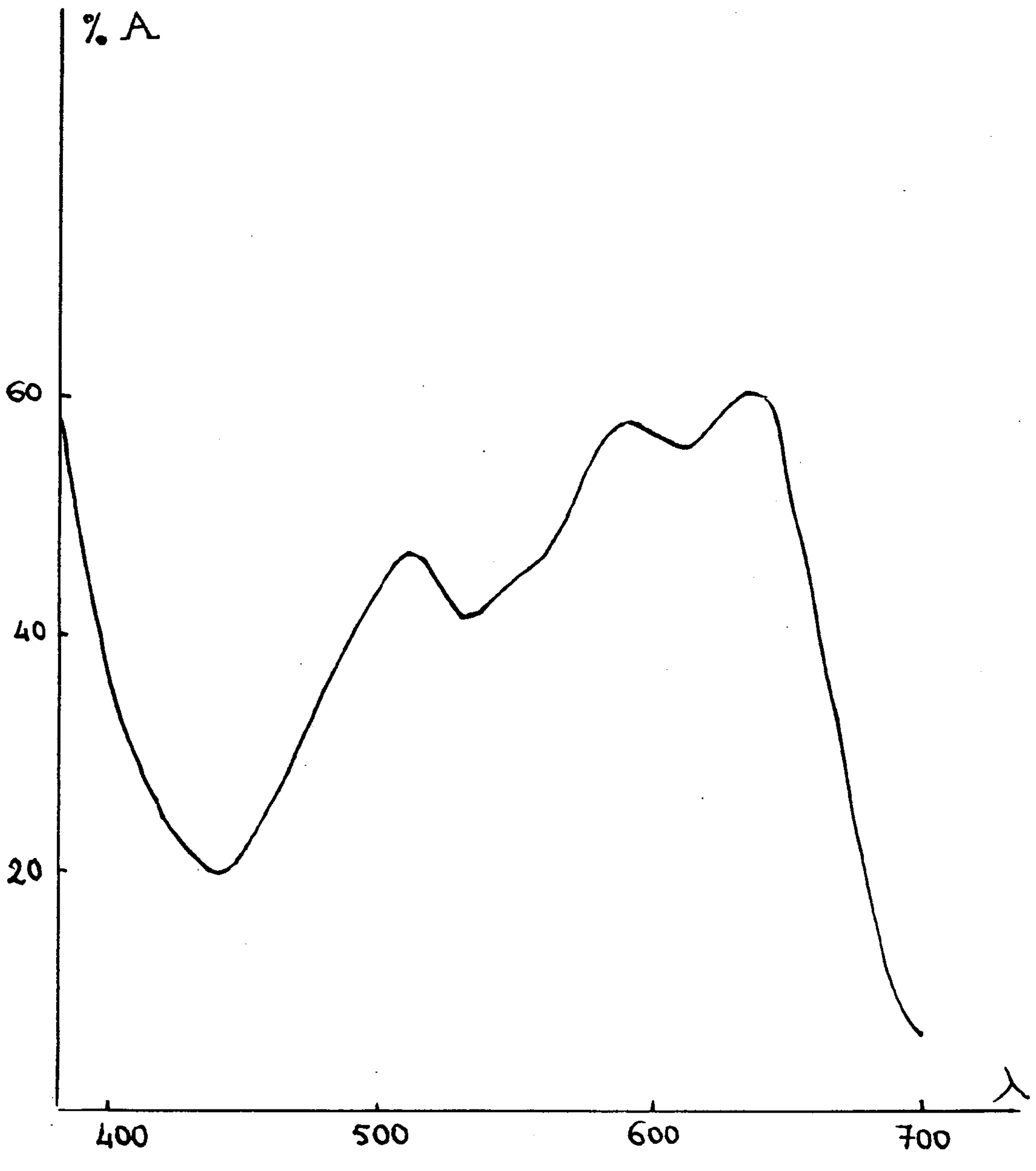
**11.** Photographic material comprising a support and on at least one side thereof at least one silver halide light-sensitive emulsion layer from an emulsion according to any of claims 1 to 10.

**12.** Photographic material according to claim 11 wherein the material has an amount of water absorption of at most 10 g/$m^2$ at the emulsion side.

**13.** Photographic material according to claim 11 or 12 wherein the said material is an X-ray photographic material.

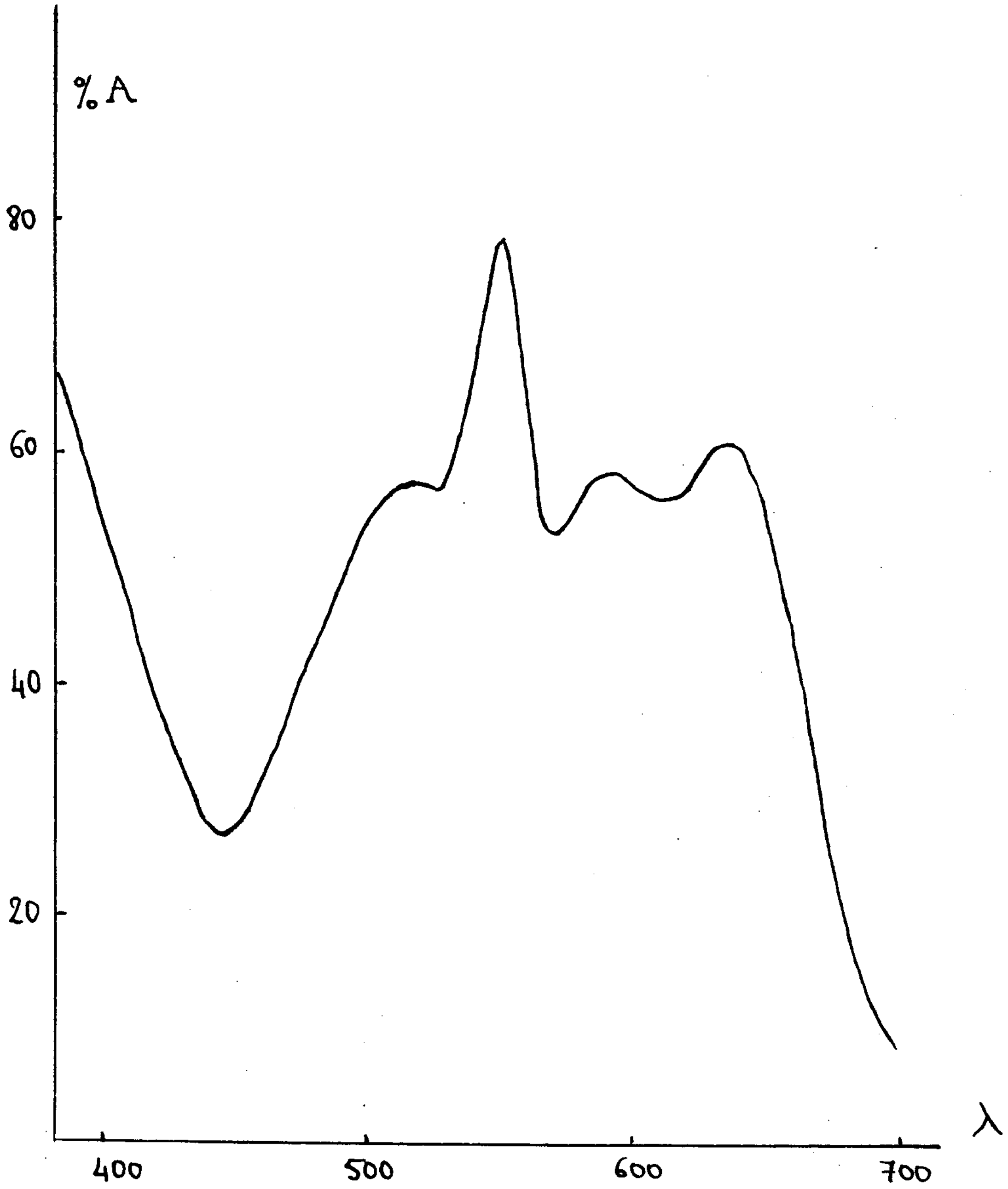
**14.** Photographic material according to claim 13 wherein said photographic material is a double side coated material with a cross-over percentage of less than 40% in the absence of an antihalation undercoating.

FIG 1



Wavelength in nanometer

FIG 2



Wavelength in nanometer

European Patent
Office

# EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0651

## 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,Y | EP-A-0 535 467 (EASTMAN KODAK COMPANY)<br>* page 10, line 19 - line 23; claims 14,17 * | 1-14 | G03C1/005 |
| D,Y | EP-A-0 534 325 (EASTMAN KODAK COMPANY)<br>* claims; example 9 * | 1-14 | |
| D,A | EP-A-0 534 395 (EASTMAN KODAK COMPANY)<br>* examples 1,3-5,10 * | 1-14 | |
| X | PATENT ABSTRACTS OF JAPAN<br>vol. 16 no. 457 (P-1426) ,22 September 1992<br>& JP-A-04 161947 (FUJI PHOTO FILM COMPANY LTD.) 5 June 1992,<br>* abstract *<br>& WPI (Derwent) AN 92-238711 | 1-14 | |
| P,A | EP-A-0 620 479 (EASTMAN KODAK COMPANY)<br>* the whole document * | 1-14 | 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 | 10 August 1995 | Buscha, A |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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