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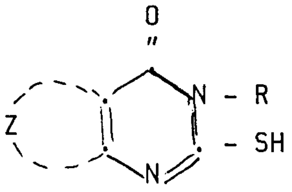
(54) Stabilization of tabular grains by pyrimidine derivatives.

(57) A photographic element is disclosed containing a silver halide emulsion comprising tabular grains having an average aspect ratio of at least 4:1, which is stabilized by a mercapto-substituted pyrimidine derivative corresponding to the general formula :



wherein :

R = hydrogen, a saturated or olefinically unsaturated aliphatic group or aryl;

Z = the ring members required for completing a condensed benzene, cyclopentene or cyclohexene ring, or a heterocyclic ring selected from the group consisting of pyridine, tetrahydropyridine, pyrimidine, pyrrole, furan, thiophene, oxazole, isoaxazole, imidazole or pyrazole ring;
and wherein R or Z contains at least one carboxy or sulfo group.

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FIELD OF THE INVENTION

The present invention relates to photographic silver halide emulsion technology and more specifically to the stabilization of tabular silver halide emulsion grains.

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 4,063,951, Lewis US 4,067,739 and Maternaghan US 4,150,994, US 4,184,877 and US 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 Sep. 30, 1982 and issued in 1984 tabular grains with high aspect ratio and their advantages in photographic applications are described. So Wilgus US 4,434,226 discloses tabular silver bromoiodide grains having a thickness less than 0.3 micron, a diameter of at least 0.6 micron and an average aspect ratio greater than 8:1 and accounting for at least 50 percent of the total projected area of all the emulsion grains. Kofron US 4,439,520 discloses similar grains which are spectrally sensitized. Abbott US 4,425,425 describes radiographic materials containing tabular grains with aspect ratio of at least 8:1 and Abbott US 4,425,426 discloses similar grains with an aspect ratio between 5:1 and 8:1. Solberg US 4,433,048 protects tabular silver bromoiodide grains with inhomogeneously distributed iodide. 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 certain spectral sensitizers can be adsorbed per mole silver halide compared to classical globular grains. As a consequence such spectrally sensitized tabular grains show a wide separation between their blue speed and minus blue speed. Sharpness of photographic images can be improved using tabular grains thanks to their lower light scattering properties again compared to conventional globular emulsion grains. In color negative materials the conventional sequence of the light sensitive layers can be altered and the yellow filter layer can be omitted. In developed black-and-white images high covering power is obtained even at high hardening levels; alternatively reduced silver halide coverages can be achieved if wanted resulting again in improved sharpness. In the especially important application field of radiographic materials where highly sensitive radiographic emulsions are coated on both sides of a transparent support the high light absorption of tabular grains in the spectrally sensitized region effectively reduces the "cross-over" which is the dominant factor for sharpness in a screen-film pair. The "cross-over" is a measure of the photographic reponse of the respective emulsion layers to the exposure from the screen located at the opposite side of the double coated film. This emission has penetrated the second emulsion layer and the support, resulting in a reduced sharpness of the finally obtained radiographic image.

Like conventional emulsions tabular grain emulsions need to be stabilized by antifoggants or stabilizers which minimize the fog increase during the processing of freshly coated photographic elements and/or the fog increase during extended storage periods of the said elements. Numerous classes of chemical compounds can be added as fog-inhibiting agent or stabilizer to conventional silver halide emulsions. 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, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione and oxazoline-thione. A especially useful class of compounds constitutute the azaindenes, e.g. triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58 and the azaindenes disclosed by Heimbach in US 2,444,607, 2,444,609, 2,449,225 and 2,450,397. The best commonly known and most widely used azaindene is 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, furtheron abbreviated as TAI. Other classes include triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JA-Appl. 75-39537, and GB 1,500,278 and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide compounds.

A widely used class of stabilizers is the class of mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole. A set of specific substituted 1-phenyl-mercaptotetrazoles is disclosed as stabilizers for tabular grain emulsions in US 4,888,273.

A general survey of stabilizers and antifoggants is given in Research Disclosure N° 17643 (1978), Chapter VI.

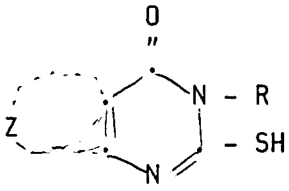
Particular problems arise in trying to stabilize highly sensitive silver bromoiodide or bromide tabular grains. Several of the familiar classes of stabilizers, e.g. mercapto-compounds, tend to desensitize the tabular grains too strongly in the concentration range where they are effective as stabilizers. Tetraazaindenes too are deficient in stabilizing high aspect ratio tabular grains, as was stated already in US 4,888,273, cited above. Experimental evidence shows that tetraazaindenes, e.g. TAI partially desorb spectral sensitizers from the grain surface, deteriorating in this way the speed in the corresponding spectral region, and in the case of double coated radiographic elements, increasing the cross-over due to a hypsochromic spectral shift of the desorbed green spectral sensitizer in the gelatin phase. Lowering the tetraazaindene concentration renders the stabilization ineffective. This problem with tetraazaindene stabilization gets more important in the case of low iodide content of the silver bromoiodide grains and is utmost severe with silver bromide emulsions containing no iodide at all. However, for application in double-side coated radiographic materials, tabular grains with minor or no iodide content are preferred because of their faster development and fixation rate compared to emulsions containing substantial amounts of iodide. The desorption of spectral sensitizer is partially overcome by adding at the finalling stage of the emulsion preparation a certain amount of a soluble iodide salt but in this case the grain surface is partially converted to AgBrI which results in an inferior sensitivity.

It is an object of the present invention to provide an effective stabilization system for tabular grains.

It is a further object of the present invention to stabilize effectively highly sensitive silver bromoiodide and silver bromide tabular grain emulsions without deteriorating the cross-over percentage, when the emulsion is double-side coated in a radiographic element.

SUMMARY OF THE INVENTION

Tabular grains, having a minimal average aspect ratio of 4:1, and accounting for at least 50 % of the total projected area of all the emulsion grains are effectively stabilized with a mercapto-substituted pyrimidine derivative represented by the following general formula :



wherein :

R = hydrogen, a saturated or olefinically unsaturated aliphatic group or aryl;

Z = the ring members required for completing a condensed benzene, cyclopentene or cyclohexene ring, or a heterocyclic ring selected from the group consisting of pyridine, tetrahydropyridine, pyrimidine, pyrrole, furan, thiophene, oxazole, isoaxazole, imidazole or pyrazole ring;

on the condition that R or Z contains at least one carboxy or sulfo group.

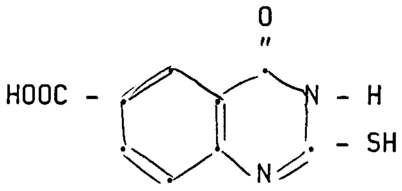
In a preferred embodiment the stabilizer of use according to the invention is combined with another stabilizer of the tetraazaindene type e.g. 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI).

Although the compounds of the present invention were already known in the art from US 3,692,527 cited above, their specific and surprising effectiveness for stabilizing tabular grains, surpassing more familiar classes of stabilizers is for the first time recognized and disclosed. It was further very surprising to discover that partial or total replacement of a tetraazaindene stabilizer by a compound according to the invention could overcome the desorption of spectral sensitizer caused by the said tetraazaindene.

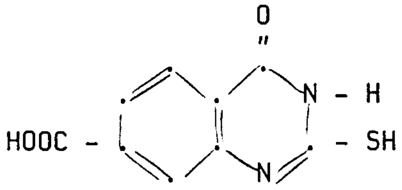
DETAILLED DESCRIPTION OF THE INVENTION

Representative examples according to the general formula of the stabilizers used according to the present invention include following compounds :

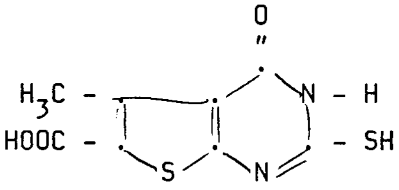
Compound 1



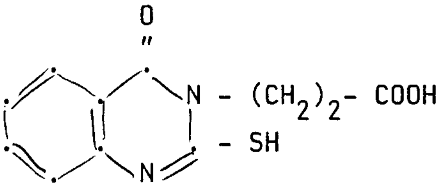
Compound 2



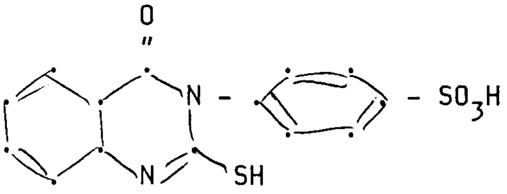
Compound 3



Compound 4



Compound 5



The most effective stabilizing agent of these specific examples is Compound 1.

The stabilizers used according to the present invention can be added to a processing solution, e.g. a development bath, but preferably they are added to the photographic material itself. They can be added to any of the hydrophylic colloid layers of the photographic material, e.g. a non-light-sensitive intermediate layer, but preferably they are contained in the light-sensitive emulsion layer(s) where they are most easily adsorbed to the tabular silver halide grains in order to exercise properly their stabilizing function. They can be added in the form of an aqueous solution or a solution in an organic solvent, e.g. a methanolic solution, or in the form of a dispersion, e.g. a gelatineous dispersion possibly containing high-boiling oilformers. They are present in a concentration ranging preferably between 10^{-7} and 10^{-3} mole per mole silver halide.

A compound according to the present invention can be used as the sole stabilizing agent or it can be combined with any other representative substance of other known stabilizer classes. Preferably it is combined with a tetraazaindene stabilizer, e.g. 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI). This tetrazaindene stabilizer is preferably present in a concentration ranging from 10^{-6} to 10^{-3} mole per mole silver halide.

The photographic tabular silver halide emulsions can be used in various types of photographic elements such as e.g. in photographic elements for graphic arts, for so-called amateur or professional still black-and-white and color photography, diffusion transfer reversal photographic elements, low-speed duplicating elements or high-speed camera sensitive elements and in motion picture recording. In a preferred embodiment of the present invention the emulsions are incorporated in a highly sensitive radiographic element.

The photographic element can contain one single emulsion layer or it can be built up by two or even more emulsion layers. In the case of color photography the material contains blue, green and red sensitive layers each of which can be single or multiple. Beside the light sensitive emulsion layer(s) the photographic material can contain several non-light sensitive layers, e.g. a protective layer, one or more backing layers, one or more subbing layers, and one or more intermediate layers. In the preferred embodiment of a radiographic element an emulsion layer is provided on both sides of a transparent support covered on each side by a protective layer.

The halide composition of the tabular silver halide emulsions used according to the present invention is not specifically limited and may be any composition selected from e.g. silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, and silver chlorobromoiodide. However in the preferred embodiment of a highly sensitive radiographic material a tabular silver bromoiodide emulsion is used, most preferably with a low iodide content up to 1 % or no iodide at all.

The tabular emulsion grains can be prepared by any method known in the art, e.g. by the methods disclosed in Research Disclosure, Vol 225, Jan 1983, Item 22534 cited above or by any similar or other method. Their minimal average aspect ratio is 4:1. Preferably their minimal average diameter is 0.6 micron and their maximal average thickness is 0.3 micron.

The emulsion can be desalted in the usual ways e.g. by dialysis, by flocculation and re-dispersing, or by ultrafiltration.

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 tabular silver halide particles of the photographic emulsions to be used according to the present invention can be monodisperse or heterodisperse.

The tabular silver halide emulsions in connection with the present invention can be chemically sensitized as described e.g. in "Chimie et Physique Photographique" by P. Glafkides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature chemical sensitization can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines. The emulsions can be sensitized also by means of gold-sulphur ripeners or by means of reductors e.g. tin compounds as described in GB 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds.

The tabular silver halide emulsions can be spectrally sensitized with methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes and complex merocyanine dyes. A survey of useful chemical classes of spectral sensitizing dyes and specific useful examples in connection with tabular grains is given in the already cited Research Disclosure Item 22534.

In classical emulsion preparation spectral sensitization traditionally follows the completion of chemical sensitization. However, in connection with tabular grains, it is specifically considered that spectral sensitization can occur simultaneously with or even precede completely the chemical sensitization step.

In the preferred embodiment of a radiographic element green sensitization is preferred in connection with the actual tendency in medical X-ray practice to use screens containing green light emitting phosphors. In this case preferred green sensitizing compounds include anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(3-sulphobutyl)-oxacarbocyanine and the sulfopropyl containing analogous compound.

It is specifically contemplated that epitaxial deposition can occur at any stage of the emulsion preparation at the surface of the tabular grains, e.g by the addition of soluble silver salts or by the addition of very fine silver halide grains capable of Ostwald ripening. Epitaxial deposition at selected edge or corner sites is preferred. In this case the presence of a so-called site director, e.g. iodide ions can be beneficial.

Besides the silver halide another essential component of a light-sensitive emulsion layer is the binder. The binder is a hydrophilic colloid, preferably gelatin. Gelatin can, however, be replaced in part or integrallly by synthetic, semi-synthetic, or natural polymers. Synthetic substitutes for gelatin are e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, polyacrylamide, polyacrylic acid, and derivatives thereof, in particular copolymers thereof. Natural substitutes for gelatin are e.g. other proteins such as zein, albumin and casein, cellulose, saccharides, starch, and alginates. In general, the semisynthetic substitutes for gelatin are modified natural products e.g. gelatin derivatives obtained by conversion of gelatin with alkylating or acylating agents or by grafting of polymerizable monomers on gelatin, and cellulose derivatives such as hydroxyalkyl cellulose, carboxymethyl cellulose, phthaloyl cellulose, and cellulose sulphates.

The gelatin can be lime-treated or acid-treated gelatin. 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).

The binder of the photographic element, especially when the binder used is gelatin, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1,3-vinylsulphonyl-2-propanol, 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 binders can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US 4,063,952.

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.

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

The photographic element 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.

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

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. In the preferred embodiment of a medical radiographic element the two emulsion layers are preferably coated on both sides of a transparent blue colored poly(ethylene terephthalate) film.

The photographic material containing tabular grains stabilized according to the present invention can be image-wise exposed by any convenient radiation source in accordance with its specific application. For the preferred embodiment of green sensitized X-ray materials, suitable commercially available green light emitting screens are KODAK LANEX and AGFA CURIX ORTHO.

The photographic elements in connection with the present invention are preferably processed in an automatically operated apparatus. For the case of the radiographic application commercially available X-ray material processors are CURIX U 242, marketed by AGFA-GEVAERT N.V. and KODAK RP-X-OMAT M6A-N, marketed by EASTMAN KODAK Co.

The following example illustrates the invention without however limiting it thereto.

EXAMPLE

1.1 Preparation of emulsion samples :

To a vessel containing 3180 ml of deionized water, 18.54 g of KBr and 12.5 g of inert gelatin at pH 5.8 and 70 °C were added 25 ml of a 2.94 molar $AgNO_3$ solution and 25 ml of a 2.94 molar KBr solution in 28 seconds by a double jet precipitation technique. Then 475 ml of a solution containing 47.5 g of phtaloylgelatin were added followed by a physical ripening period of 10 min. In order to adjust the pBr to 2.03 a 2.94 molar solution of $AgNO_3$ was added at a rate of 5 ml/s during 564 seconds. Thereupon 928 ml of a 2.94 molar $AgNO_3$ solution and a 2.94 molar KBr solution were added simultaneously at a rate being initially 5 ml/s and increasing linearly to 49 ml/s. The pBr was maintained during this precipitation stage at a fixed value of 2.03. Finally the pH was adjusted to 3.5 by means of a sulphuric acid solution and the temperature was decreased to 40 °C. After washing 160 g of inert gelatin was added and the pH and pAg were adjusted to 5.5 and 7.64 respectively.

The thus obtained tabular grains had an average thickness of 0.20 micron and an average aspect ratio of 6.6 as determined by the method described by Abott et al in GB 2,110,402. Of the total projected area 80 % was covered with tabular grains.

During the next stage of the preparation the emulsion was divided in aliquot portions. Each portion was spectrally sensitized to the green spectral region with 935 mg of anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(3-sulphobutyl)-oxacarbocyanine and then chemically sensitized by means of 15.1 umole/mole $AgNO_3$ of sodium thiosulphate, 1.73 umole/mole $AgNO_3$ of chloroauric acid and 1.32 mmole/mole $AgNO_3$ of potassium thiocyanate. The time of chemical senstization was adjusted for each sample in order to obtain an optimal fog/density ratio after coating and processing. Then the emulsion samples were cooled and to each sample the desired amount of stabilizer was added (see table 1). Hereafter each emulsion sample was coated on both sides of a polyethyleneterephtalate film at a silver coverage of 2 x 3.0 g expressed as $AgNO_3/m^2$. A protective layer containing 1.1 g gelatin/m^2 was applied on both sides and as a hardener formaldehyde was used.

1.2 Evaluation of photographic properties :

The coated samples were exposed to green light having a peak emission at 545 nm through a continuous tone wedge. Part of the samples were stored at 57 °C and 34 % relative humidity in order to simulate an extended shelf life period. Processing was performed in a X-ray film processor (90 s cycle) using following processing solutions : a developing solution adjusted to pH 10.1 comprising hydrochinon, 1-phenyl-5-pyrazolidinone, potassium sulphite, 5-nitroindazole and glutaric dialdehyde as mean ingredients and a conventional fixing solution comprising ammonium thiosulphate adjusted to pH 4.3.

The cross-over percentage was determined as follows. A film-screen element, consisting of a double side coated emulsion sample in close contact with a single green emitting screen at the side of the X-ray source and a white paper replacing the second screen at the other side was exposed to varying doses of X-rays. After processing these elements the sensitometric curves (density as a function of the X-ray dose) were determined. From the difference in sensitivity, log E, between those two layers the % cross-over was calculated according to the following equation :

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

Table 1 illustrates the sensitometric results of the stabilization of the described tabular grains by 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) and 2-mercapto-4-hydroxy-6-carboxy-quinazoline (compound 1), a stabilizer of the present invention. Sensitivities are expressed as relative arithmetic values, sample 1 having reference value 100. Table 2 presents the procentual cross-over values.

TABLE 1

Sample No	Conc. TAI mmol/mole Ag	Conc. COMP. 1 mmole/mole Ag	Fog fresh	Sensitivity fresh	Fog 3 d 57/34
1	1.20	0	0.030	100	0.337
2	2.40	0	0.023	75	0.122
3	1.20	0.225	0.009	100	0.014
4	2.40	0.225	0.008	91	0.015

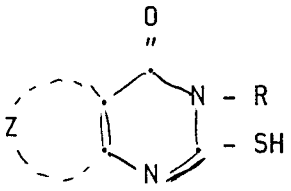
TABLE 2

Sample No	% cross-over	remark
1	39	comparison
2	57	comparison
3	41	invention
4	52	invention

The results of table 1 and 2 show that the use of TAI as sole stabilizer cannot limit the fog increase after conditioning the materials for 3 days at 57 °C and 34 % RH without severely deteriorating the cross-over. On the contrary the quinazoline derivative according to the present invention, combined with TAI, significantly reduces the fog increase after conditioning without significant variation in cross-over percentage.

Claims

1. Photographic material comprising a support and at least one light sensitive emulsion layer containing tabular silver halide grains having an average aspect ratio of at least 4:1 and accounting for at least 50 % of the total projected area of all the grains characterized in that said emulsion is stabilized by a mercapto-sustituted pyrimidine derivative represented by the general formula :



wherein :

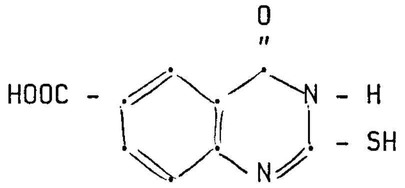
R = hydrogen, a saturated or olefinically unsaturated aliphatic group or aryl;

Z = the ring members required for completing a condensed benzene, cyclopentene or cyclohexene ring, or a heterocyclic ring selected from the group consisting of pyridine, tetrahydropyridine, pyrimidine, pyrrole, furan, thiophene, oxazole, isoaxazole, imidazole or pyrazole ring;

and wherein R or Z contains at least one carboxy or sulfo group.

2. Photographic material according to claim 1 characterized in that said stabilizer is the following

quinazoline derivative :



3. Photographic material according to claims 1 and 2 characterized in that said stabilizer is added to the emulsion in a concentration ranging from 10^{-7} mole to 10^{-3} mole per mole silver halide.

4. Photographic material according to any of claims 1 to 3 characterized in that said stabilizer is combined with a stabilizer of the tetraazaindene type.

5. Photographic material according to claim 4 characterized in that said tetraazaindene stabilizer is 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene.

6. Photographic material according to any of claims 1 to 5 characterized in that the grains of said tabular emulsion exhibit a minimal average diameter of 0.6 micron and maximal average thickness of 0.3 micron.

7. Photographic material according to any of claims 1 to 6 characterized in that said photographic material is a radiographic X-ray recording material.

8. Photographic material according to claim 7 characterized in that said radiographic material comprises a high speed tabular bromoiodide emulsion coated on both sides of a transparent support.

9. Photographic material according to claim 8 characterized in that said radiographic material is green sensitized.

10. Photographic material according to any of claims 1 to 9 characterized in that said tabular grains have undergone epitaxial deposition on their surface.

European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 20 1842

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.5)
D,Y	US-A-4 425 426 (T. ABBOTT et al.) * claims; column 24, line 27 - column 26, line 22 * – – –	1-9	G 03 C 1/035 G 03 C 1/34
Y	FR-A-2 073 677 (AGFA) * claims; page 12, line 33 - page 13, line 32 *; & US-A-3692527 (cat. D) – – –	1-9	
A	EP-A-0 244 718 (3M) * page 10, dye 5; page 11, line 1 - page 12, line 10 * – – –	1-10	
A	JOURNAL OF IMAGING SCIENCE vol. 32, no. 4, July/August 1988, pages 160-177, Springfield, VA, US; J.E. MASKASKY: "Epitaxial Selective Site Sensitization of Tabular Grain Emulsions" * whole paper * – – – – –	10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
G 03 C 1/00 G 03 C 5/00

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
Berlin	05 March 91	STOCK H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same catagory
A : technological background
O : non-written disclosure
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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