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(54) **Process for chemically sensitizing a green-sensitive silver halide photographic emulsion and photographic material containing said emulsion**

Verfahren zur chemischen Sensibilisierung einer grün-empfindlichen Silberhalogenidemulsion und photographisches Material beinhaltend eine solche Emulsion

Procédé de sensibilisation chimique des émulsions photographiques à l'halogénure d'argent sensible à la lumiere verte, et materiau photographique contenant une telle émulsion

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**DE-A- 3 923 958** **US-A- 4 849 327**

- **"Photographic silver halide emulsions, preparations, addenda, processing and systems" , RESEARCH DISCLOSURE, KENNETH MASON PUBLICATIONS, HAMPSHIRE, GB, NR. 17643, PAGE(S) 1-37 XP002240417 ISSN: 0374-4353 * column III - column IV ***

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

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## Description

**[0001]** The present invention refers to a process for chemically sensitizing a silver halide photographic emulsion, to a green-sensitive silver halide emulsion and to a photographic material containing said emulsion.

**[0002]** The manufacturing process of photographic materials includes the steps related to the preparation of silver halide emulsions which comprises, among the others, emulsion making, chemical and/or optical emulsion sensitization and emulsion coating.

**[0003]** Processes for chemically sensitize silver halide emulsions are well known in the art and they include, for example, the use of sulfur, selenium or gold sensitizers. P-toluenethiosulfonate is a well-known sulfuring agent, as described, for example, in US Patent Nos. 6,017,684 and 5,573,901. A sulfur sensitization is usually carried out by adding a sulfur sensitizer to an emulsion and stirring it for a predetermined time at an elevated temperature, preferably 40°C or higher. Known sulfur sensitizers used for the sulfur sensitization are for example, thiosulfate, thioureas, allylisothiacyanate, cystine, p-toluenethiosulfonate, and rhodanine. European Patent application No. 576,910 discloses tabular silver bromide grains having a thickness lower than 0.4 mm and an aspect ratio lower than 8:1 prepared in the presence of a deionized gelatin. The obtained emulsion was optically sensitized to green light with a cyanine dye and chemically sensitized with sodium p-toluenethiosulfonate, sodium p-toluene-sulfinate and benzothiazoleiodoethylate.

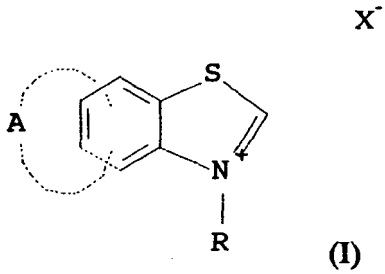
**[0004]** During the manufacturing process of photographic material, when the silver halide emulsion preparation is completed, the emulsion must be coated onto a support base of a photographic material together with auxiliary coating solutions, such as, for example, coating solutions containing dye-forming couplers, sensitizing dyes, ultraviolet absorbers and the like. However, in many cases, a variable period of time (herein defined as "coating waiting time" and ranging from some minutes to several hours) can pass from the moment in which the emulsion is ready to be coated onto the photographic support and the effective time in which the emulsion will be coated. This is mainly due to manufacturing problems, arising from the fact that not always the emulsions and all the coating solutions are ready to be coated at the same time or from other technical industrial problems during manufacturing process. A problem which can arise during said coating waiting time is the change in photographic properties which occurs to silver halide emulsion, due to chemical reactions of agents contained in the coating solutions activated by a synergic action of relative high temperature (about 40-45°C) and long coating waiting time.

**[0005]** Benzo-bis-thiazolium compounds are known in the art. In fact, for example, US Patent No. 4,849,327 discloses a photographic material comprising a silver halide emulsion associated with a benzo-bis-thiazolium quaternary salt antifogging agent to inhibit fog formation and US Patent No. 5,024,928 discloses a color reversal photographic material comprising, in a blue-sensitive silver halide emulsion layer, the combination of a specific monomethine cyanine spectral sensitizing dye and a specific benzo-bis-thiazolium quaternary salt to improve yellow color reproducibility.

**[0006]** Despite the attempts to provide photographic emulsions which maintain photographic speed and control fog growth upon storage, after that the emulsion has been coated onto a photographic support, the art has not yet provided a method which is able to maintain said photographic characteristics during the coating waiting time, that is after the photosensitive emulsion has been chemically sensitized and before it has been coated onto a photographic support, together with the auxiliary coating solutions.

**[0007]** A similar problem has been solved in US Patent No. 6,143,484, wherein a method for stabilizing a photographic coating melt by the addition of certain surfactants to a Lippmann emulsion before adding said emulsion to a photographic dispersion of an ultraviolet absorber compound is disclosed. The surfactant greatly inhibits an undesired growth in the photographic dispersion subject to large droplet formation, allowing the emulsion to show good sensitometric properties.

**[0008]** The present invention provides a process for chemically sensitizing a silver halide photographic emulsion including the addition to said emulsion, during the chemical sensitization, of a benzo-bis-thiazole quaternary salt represented by the general formula (I):




(I)

wherein R is an alkyl, or an alkinyl group having from 1 to 5 carbon atoms, A represents the atoms necessary to complete a benzo-bis-thiazole nucleus and $X^-$ is an anion.

**[0009]** Another aspect of the present invention relates to a chemically sensitized green-sensitive silver halide emulsion comprising a benzo-bis-thiazole quaternary salt as above and to a photographic material containing in at least one light-sensitive layer said chemically sensitized green-sensitive silver halide photographic emulsion.

**[0010]** The chemically sensitized green-sensitive silver halide emulsion of the present invention has the advantage that it maintains the good sensitometric characteristics even after being maintained for a long coating waiting time.

**[0011]** The manufacturing process of silver halide elements usually comprises an emulsion-making step, a chemical and optical sensitization step, and a coating step.

**[0012]** The silver halide emulsion-making step generally comprises a nucleation step, in which silver halide grain seeds are formed, followed by one or more growing steps, in which the grain seeds achieve their final dimension, and a washing step, in which all soluble salts are removed from the final emulsion. A ripening step is usually performed between the nucleation and growing step and/or between the growing and the washing steps.

**[0013]** In the preparation of silver halide emulsions, commonly used halogen compositions of the silver halide grains can be used. Suitable silver halides include silver chloride, silver bromide, silver iodide, silver chloroiodide, silver bromoiodide, silver chlorobromoiodide and the like. However, silver bromide and silver bromoiodide are preferred silver halide compositions with silver bromoiodide compositions containing from 0 to 10 mol % silver iodide, preferably, from 0.2 to 5 mol % silver iodide, and more preferably, from 0.5 to 1.5 mol % silver iodide. The halogen composition of individual grains may be homogeneous or heterogeneous.

**[0014]** The silver halide grains of the emulsion used in the present invention may be grains having a regular crystal structure such as cube, octahedron, and tetra-decahedron, or the spherical or irregular crystal structure, or those having crystal defects such as twin plane, or those having a tabular form, or the combination thereof.

**[0015]** The term "cubic grains" according to the present invention is intended to include substantially cubic grains, that is grains which are regular cubic grains bounded by crystallographic faces (100), or which may have rounded edges and/or vertices or small faces (111), or may even be nearly spherical when prepared in the presence of soluble iodides or strong ripening agents, such as ammonia. Particularly good results are obtained with silver halide grains having average grain sizes in the range from 0.2 to 3 μm, more preferably from 0.4 to 1.5 μm. Preparation of silver halide emulsions comprising cubic silver iodobromide grains is described, for example, in Research Disclosure, Vol. 184, Item 18431, Vol. 176, Item 17644 and Vol. 308, Item 308119.

**[0016]** Other silver halide emulsions according to this invention are those which employ one or more light-sensitive tabular grain emulsions. The tabular silver halide grains contained in the emulsion used in this invention have an average diameter:thickness ratio (often referred to in the art as aspect ratio) of at least 2:1, preferably 2:1 to 20:1, more preferably 3:1 to 14:1, and most preferably 3:1 to 8:1. Average diameters of the tabular silver halide grains suitable for use in this invention range from 0.3 μm to 5 μm, preferably 0.5 μm to 3 μm, more preferably 0.8 μm to 1.5 μm. The tabular silver halide grains suitable for use in this invention have a thickness of less than 0.4 μm, preferably less than 0.3 μm and more preferably less than 0.2 μm.

**[0017]** The tabular grain characteristics described above can be readily ascertained by procedures well known to those skilled in the art. The term "diameter" is defined as the diameter of a circle having an area equal to the projected area of the grain. The term "thickness" means the distance between two substantially parallel main planes constituting the tabular silver halide grains. From the measure of diameter and thickness of each grain the diameter:thickness ratio of each grain can be calculated, and the diameter:thickness ratios of all tabular grains can be averaged to obtain their average diameter:thickness ratio. By this definition the average diameter:thickness ratio is the average of individual tabular grain diameter:thickness ratios. In practice, it is simpler to obtain an average diameter and an average thickness of the tabular grains and to calculate the average diameter:thickness ratio as the ratio of these two averages. Whatever the used method may be, the average diameter:thickness ratios obtained do not greatly differ.

**[0018]** In the silver halide emulsion layer containing tabular silver halide grains, at least 15%, preferably at least 25%, and, more preferably, at least 50% of the silver halide grains are tabular grains having an average diameter:thickness ratio of not less than 2:1. Each of the above proportions, "15%", "25%" and "50%" means the proportion of the total projected area of the tabular grains having a diameter:thickness ratio of at least 2:1 and a thickness lower than 0.4 μm, as compared to the projected area of all of the silver halide grains in the layer.

**[0019]** Silver bromoiodide grains having an inner core and a plurality of shells can be used in the present invention. The inner core generally consists essentially of silver bromide or silver bromoiodide, while the plurality of shells generally consists essentially of silver bromide or silver bromoiodide having different silver halide compositions. The silver iodide content of the inner core is preferably in the range of from 0 to 20 mol% relative to the total silver halide content of the inner core phase, more preferably from 0 to 10 mol%, and most preferably from 0 to 5 mol%. The silver iodide content of each shell is in the range of from 0 to 40 mol%, preferably from 0 to 20 mol% relative to the total silver halide content of the shell. The plurality of shells generally comprises at least two shells having different silver halide composition and the number of shells surrounding the inner core preferably ranges from two to four, as described, for example, in US Patent No. 6,258,522. The silver content of the core and the plurality of shells relative to the total silver content of the grain can have different values depending on the number of shells representing the plurality of shells.

**[0020]** It is known that photosensitive silver halide emulsions can be formed by precipitating silver halide grains in an aqueous dispersing medium comprising a binder, gelatin preferably being used as a binder.

**[0021]** The silver halide grains may be precipitated by a variety of conventional techniques. The silver halide emulsion can be prepared using a single-jet method, a double-jet method, or a combination of these methods or can be matured using, for instance, an ammonia method, a neutralization method, an acid method, or can be performed an accelerated or constant flow rate precipitation, interrupted precipitation, ultrafiltration during precipitation, etc. References can be found in Trivelli and Smith, The Photographic Journal, Vol. LXXIX, May 1939, pp. 330-338, T.H. James, The Theory of The Photographic Process, 4th Edition, Chapter 3, US Patent Nos. 2,222,264, 3,650,757, 3,917,485, 3,790,387, 3,716,276, 3,979,213, Research Disclosure, Dec. 1989, Item 308119, and Research Disclosure, Sept. 1976, Item 14987.

**[0022]** One common technique is a batch process commonly referred to as the double-jet precipitation process by which a silver salt solution in water and a halide salt solution in water are concurrently added into a reaction vessel containing the dispersing medium.

**[0023]** In the double jet method, in which alkaline halide solution and silver nitrate solution are concurrently added in the gelatin solution, the shape and size of the formed silver halide grains can be controlled by the kind and concentration of the solvent existing in the gelatin solution and by the addition speed. Double-jet precipitation processes are described, for example, in GB 1,027,146, GB 1,302,405, US 3,801,326, US 4,046,376, US 3,790,386, US 3,897,935, US 4,147,551, and US 4,171,224.

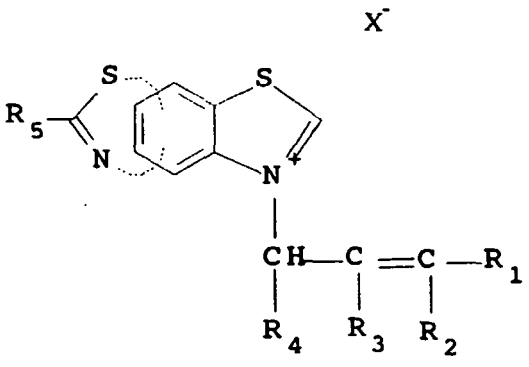
**[0024]** The single jet method in which a silver nitrate solution is added in a halide and gelatin solution has been long used for manufacturing photographic emulsion. In this method, because the varying concentration of halides in the solution determines which silver halide grains are formed, the formed silver halide grains are a mixture of different kinds of shapes and sizes.

**[0025]** In order to avoid soluble salts in the emulsion layers of a photographic material from crystallizing out after coating and other photographic or mechanical disadvantages (stickiness, brittleness, etc.), the soluble salts formed during precipitation have to be removed.

**[0026]** In preparing the silver halide emulsions used in the present invention, a wide variety of hydrophilic dispersing agents for the silver halides can be employed. As hydrophilic dispersing agent, any hydrophilic polymer conventionally used in photography can be advantageously employed including gelatin, a gelatin derivative such as acylated gelatin, graft gelatin, etc., albumin, gum arabic, agar agar, a cellulose derivative, such as hydroxyethylcellulose, carboxymethylcellulose, etc., a synthetic resin, such as polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamide, etc. Other hydrophilic materials useful known in the art are described, for example, in Research Disclosure, Vol. 308, Item 308119, Section IX.

**[0027]** In the process of the present invention, the chemical sensitization of the above described silver halide emulsion is performed by adding a benzo-bis-thiazole quaternary salt of previous formula I. In said formula, R is a low alkyl group having 1 to 5 carbon atoms, such as a methyl group, an ethyl group, a propyl group, an iso-propyl group, a butyl group, an isobutyl group, a tertiary-butyl group, a normal pentyl group or a tertiary amyl group; or R is a low alkenyl group having 1 to 5 carbon atoms, that is a linear or branched hydrocarbon radical containing at least one carbon--carbon double bond, such as, for example, vinyl groups and allyl group, or R is a low alkinyl group having 1 to 5 carbon atoms, that is a linear or branched hydrocarbon radical containing at least one carbon-carbon triple bond, such as, for example, a propargyl group and a butynyl group.

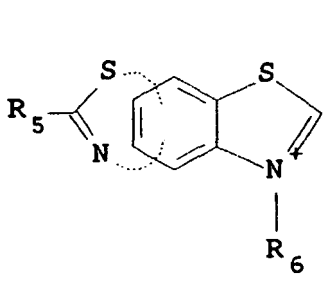
**[0028]** In one preferred embodiment, the benzo-bis-thiazole quaternary salt used in the present invention is represented by the following general formula (II):



(II)

wherein $R_1$, $R_2$, $R_3$, $R_4$ and $R_5$ is hydrogen atom or a low alkyl group having 1 to 5 carbon atoms and $X^-$ is an anion.

**[0029]** In another preferred embodiment, the benzo-bis-thiazole quaternary salt used in the present invention is represented by the following general formula (III):



(III)

wherein $R_5$ is hydrogen atom or a low alkyl group having 1 to 5 carbon atoms, $R_6$ is a low alkyl group having 1 to 3 carbon atoms, and $X^-$ is an anion.

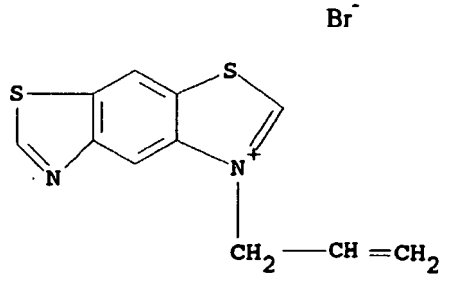
**[0030]** In the previous formulas (I) to (III), the non-quaternized thiazole group may be fused to the benzene ring by linking the nitrogen atom and the sulphur atom to the positions 3, 4, 5, or 6 of the benzene ring. By this way, the nitrogen atom may be linked to the 3-position and the sulphur atom to the 4-position of the benzene ring or viceversa (thus obtaining a benzo(1,2-d:4,3-d')-bisthiazole quaternary salt and a benzo-(1,2-d:3,4-d')-bisthiazole quaternary salt, respectively), or the nitrogen atom may be linked to the 4-position and the sulphur atom to the 5-position of the benzene ring or viceversa (thus obtaining a benzo-(1,2-d:5,4-d')-bisthiazole quaternary salt and a benzo-(1,2-d:4,5-d')- bisthiazole quaternary salt, respectively) or the nitrogen atom may be linked to the 5-position and the sulphur atom to the 6-position of the benzene ring or viceversa (thus obtaining a benzo-(1,2-d:6,5-d')-bisthiazole quaternary salt and a benzo-(1,2-d: 5,6-d')-bisthiazole quaternary salt, respectively).

**[0031]** Low alkyl groups represented by $R_1$, $R_2$, $R_3$, $R_4$ and $R_5$ have from 1 to 5 carbon atoms; suitable low alkyl groups are a methyl group, an ethyl group, a propyl group, an iso-propyl group, a butyl group, an isobutyl group, a tertiary-butyl group, a normal pentyl group or a tertiary amyl group. Preferably, $R_5$ is a methyl group The total number of carbon atoms of the low alkyl groups represented by $R_1$, $R_2$, $R_3$ and $R_4$, when more than one group is present, is such as not to negatively affect the properties of the benzo-bis-thiazole quaternary salts according to this invention. The low alkyl groups represented by $R_1$, $R_2$, $R_3$ and $R_4$ may have up to a maximum of 20 carbon atoms. Preferably, said total number of carbon atoms of $R_1$, $R_2$, $R_3$ and $R_4$ is less than 15, more preferably less than 10. Low alkyl groups represented by $R_6$ have from 1 to 3 carbon atoms; suitable low alkyl groups are, for example, a methyl group, an ethyl group and a propyl group.

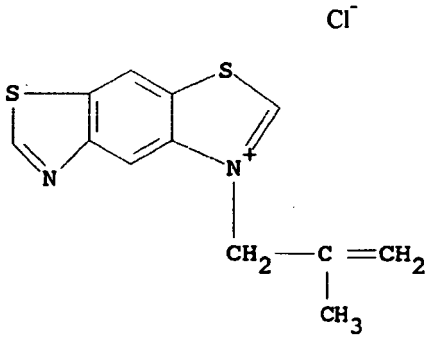
**[0032]** When the term "group", is used in this invention to describe a chemical compound or substituent, the described chemical material includes the basic group, ring or residue and that group, ring or residue with conventional substitution. Where the term "moiety" is used to describe a chemical compound or substituent, only the unsubstituted chemical material is intended to be included. For example, "alkyl group" includes not only such alkyl moiety as methyl, ethyl, butyl, octyl, stearyl, etc., but also moieties bearing substituent groups such as halogen cyano, hydroxyl, nitro, amino, carboxylate, etc. On the other hand, "alkyl moiety" includes only methyl, ethyl, stearyl, cyclohexyl, etc.

**[0033]** $X^-$ of formulas (I) to (III) above represents an acid anion (e.g. chloride, bromide, iodide, thiocyanate, methylsulfate, ethylsulfate, perchlorate, p-toluenesulfonate ions or other well-known photographically inert or harmless anions).

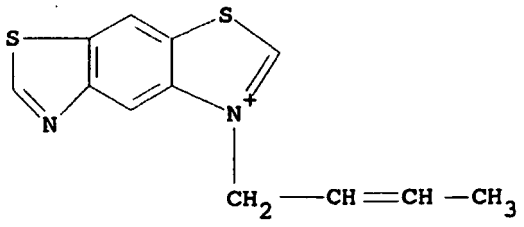
**[0034]** Typical examples of the benzo-bis-thiazole quaternary salts according to the present invention include the following:



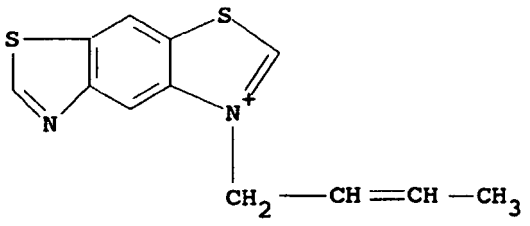
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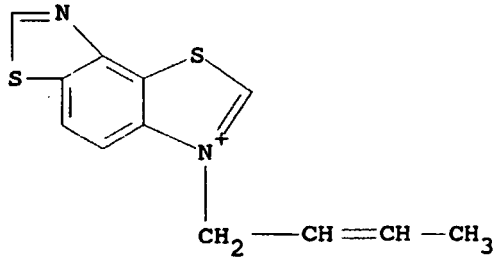
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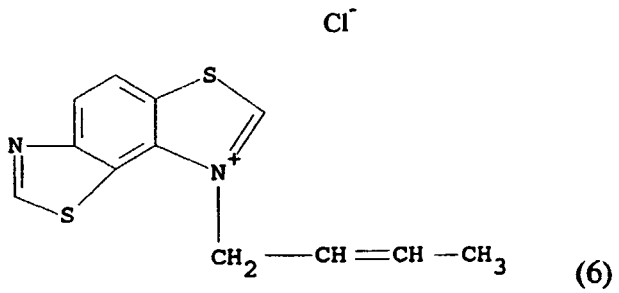
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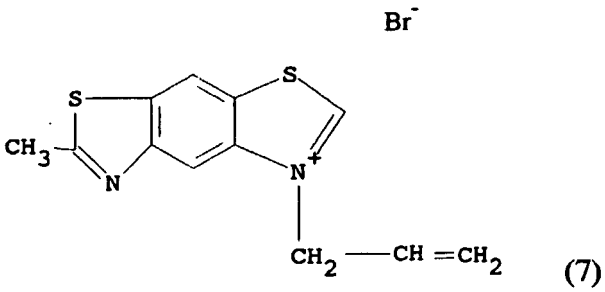
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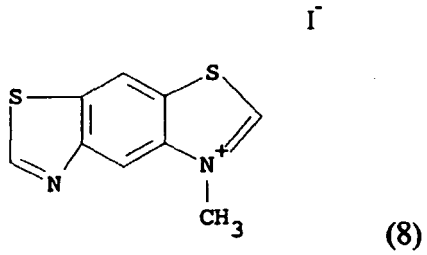
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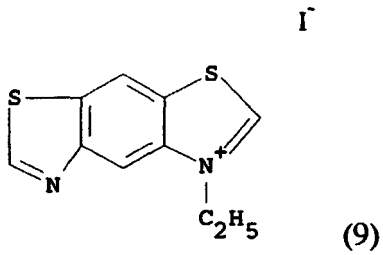
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(9)

**[0035]** The benzo-bis-thiazole quaternary salts used in the present invention can be prepared according to methods known in the art, such as described, for example, in US Patent No. 4,849,327.

**[0036]** The most useful amount of the benzo-bis-thiazole quaternary salts used in the present invention varies correspondingly with various factors, such as the silver halide composition, the nature of the other components of the emulsion, the use of the photographic element, and the like. However, useful amounts are generally in the range from 0.01 to 10 millimoles per mole of silver and preferably from 0.1 to 5 millimoles per mole of silver.

**[0037]** Preferably, the process for chemically sensitizing a silver halide photographic emulsion of the present invention further includes the addition to said emulsion of a sulfur chemical sensitizer in such an amount as will effectively increase the sensitivity of the emulsion. The amount, which depends on various conditions such as the pH value, the temperature and the size of the silver halide grains, is preferably in the range from $1x10^{-7}$ to $1x10^{-1}$ grams per mole of silver, more preferably, from $1x10^{-4}$ to $1x10^{-2}$ grams per mole of silver. In particular, the silver halide emulsions may be chemically sensitized with a sulfur sensitizer, such as thiosulfonate salts (for example, p-toluene thiosulfonate potassium salt),

sodium thiosulfate, allylthiocyanate, allylthiourea, thiosulfinic acid and its sodium salt, sulfonic acid and its sodium salt, allylthiocarbamide, thiourea, cystine, etc..

**[0038]** In the process for chemically sensitizing a silver halide photographic emulsion of the present invention, the sulfur sensitizer can be added before, during or after the addition of the benzo-bis-thiazole quaternary salt of previous formula (I). Preferably, the sulfur sensitizer is added after the addition of said benzo-bis-thiazole quaternary salt.

**[0039]** Additional useful examples of chemical sensitizers can be used, such as, for example, an active or inert selenium sensitizer; a reducing sensitizer such as stannous salt, a polyamine, etc.; a noble metal sensitizer, such as gold sensitizer, more specifically potassium aurithiocyanate, potassium chloroaurate, etc.; or a sensitizer of a water soluble salt such as for instance of ruthenium, rhodium, iridium and the like, more specifically, ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladite, etc.; each being employed either alone or in a suitable combination, as described, for example, in Research Disclosure 17643, Section III, 1978 and in Research Disclosure 308119, Section III, 1989.

**[0040]** Stabilizers such as tetraazaindenes (for example, 4-hydroxy-6-methyl-1,3,3a,7- tetraazaindene), and those described in Research Disclosure Item 308119, Section VI, can be added to the emulsion used in the present invention. Thiosulfonate and sulfinate compounds can be prepared with methods known in the art as described, for example, in Journal of Organic Chemistry, vol. 53, p. 386 (1988) and Chemical Abstracts , vol. 59, 9777e. The more preferred compounds, sodium or potassium p-toluene thiosulfonate and p-toluene sulfinate, are available on the market of chemical compounds.

**[0041]** The silver halide emulsion used in the present invention can be spectrally sensitized with dyes from a variety of classes, including the polymethyne dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines, oxonols, hemioxonols, styryls, merostyryls, and streptocyanine.

**[0042]** The cyanine spectral sensitizing dyes include, joined by a methine linkage, two basic heterocyclic nuclei, such as those derived from quinoline, pyrimidine, isoquinoline, indole, benzindole, oxazole, thiazole, selenazole, imidazole, benzoxazole, benzothiazole, benzoselenazole, benzoimidazole, naphthoxazole, naphthothiazole, naphthoselenazole, tellurazole, oxatellurazole.

**[0043]** The merocyanine spectral sensitizing dyes include, joined by a methine linkage, a basic heterocyclic nucleus of the cyanine-dye type and an acidic nucleus, which can be derived from barbituric acid, 2-thiobarbituric acid, rhodanine, hydantoin, 2-thiohydantoin, 2-pirazolin-5-one, 2-isoxazolin-5-one, indan-1,3-dione, cyclohexane-1,3-dione, 1,3-dioxane-4,6-dione, pyrazolin-3,5-dione, pentane-2,4-dione, alkylsulfonylacetonitrile, malononitrile, isoquinolin-4-one, chromane-2,4-dione, and the like.

**[0044]** One or more spectral sensitizing dyes may be used. Dyes with sensitizing maxima at wavelengths throughout the visible and infrared spectrum and with a great variety of spectral sensitivity curve shapes are known. The choice and relative proportion of dyes depends on the region of the spectrum to which sensitivity is desired and on the shape of the spectral sensitivity desired.

**[0045]** Examples of sensitizing dyes can be found in Venkataraman, The chemistry of Synthetic Dyes, Academic Press, New York, 1971, Chapter V, James, The Theory of the Photographic Process, 4th Ed., Macmillan, !977, Chapter 8, F.M.Hamer, Cyanine Dyes and Related Compounds, John Wiley and Sons, 1964.

**[0046]** The silver halide emulsion used in the present invention can be used for the manufacture of light-sensitive silver halide photographic elements, in particular color negative photographic elements, color reversal photographic elements, and the like.

**[0047]** Silver halide multilayer color photographic elements usually comprise, coated on a support, a red sensitized silver halide emulsion layer associated with cyan dye-forming color couplers, a green sensitized silver halide emulsion layer associated with magenta dye-forming color couplers and a blue sensitized silver halide emulsion layer associated with yellow dye-forming color couplers. Each layer can be comprised of a single emulsion layer or of multiple emulsion sub-layers sensitive to a given region of visible spectrum. When multilayer materials contain multiple blue, green or red sub-layers, there can be in any case relatively faster and relatively slower sub-layers. These elements additionally comprise other non-light sensitive layers, such as intermediate layers, filter layers, antihalation layers and protective layers, thus forming a multilayer structure. These color photographic elements, after imagewise exposure to actinic radiation, are processed in a chromogenic developer to yield a visible color image. The layer units can be coated in any conventional order, but in a preferred layer arrangement the red-sensitive layers are coated nearest the support and are overcoated by the green-sensitive layers, a yellow filter layer and the blue-sensitive layers.

**[0048]** Suitable color couplers are preferably selected from the couplers having diffusion preventing groups, such as groups having a hydrophobic organic residue of 8 to 32 carbon atoms, introduced into the coupler molecule in a non-splitting-off position. Such a residue is called a "ballast group". The ballast group is bonded to the coupler nucleus directly or through an imino, ether, carbon-amido, sulfonamido, ureido, ester, imido, carbamoyl, sulfamoyl bond, etc. Examples of suitable ballasting groups are described in US patent 3,892,572.

**[0049]** Said non-diffusible couplers are introduced into the light-sensitive silver halide emulsion layers or into non-light-sensitive layers adjacent thereto. On exposure and color development, said couplers give a color which is comple-

mentary to the light color to which the silver halide emulsion layers are sensitive. Consequently, at least one non-diffusible cyan-image forming color coupler, generally a phenol or an alpha-naphthol compound, is associated with red-sensitive silver halide emulsion layers, at least one non-diffusible magenta image-forming color coupler, generally a 5-pyrazolone or a pyrazolotriazole compound, is associated with green-sensitive silver halide emulsion layers and at least one non-diffusible yellow image forming color coupler, generally a acylacetanilide compound, is associated with blue-sensitive silver halide emulsion layers.

**[0050]** Said color couplers may be 4-equivalent and/or 2-equivalent couplers, the latter requiring a smaller amount of silver halide for color production. As is well known, 2-equivalent couplers derive from 4-equivalent couplers since, in the coupling position, they contain a substituent which is released during coupling reaction. 2-Equivalent couplers which may be used in silver halide color photographic elements include both those substantially colorless and those which are colored ("masked couplers"). The 2-equivalent couplers also include white couplers which do not form any dye on reaction with the color developer oxidation products. The 2-equivalent color couplers include also DIR couplers which are capable of releasing a diffusing development inhibiting compound on reaction with the color developer oxidation products.

**[0051]** The most useful cyan-forming couplers are conventional phenol compounds and a-naphthol compounds. Examples of cyan couplers can be selected from those described in US patents 2,369,929; 2,474,293; 3,591,383; 2,895,826; 3,458,315; 3,311,476; 3,419,390; 3,476,563 and 3,253,924; and in British patent 1,201,110.

**[0052]** The most useful magenta-forming couplers are conventional pyrazolone type compounds, indazolone type compounds, cyanoacetyl compounds, pyrazoletriazole type compounds, etc, and particularly preferred couplers are pyrazolone type compounds. Magenta-forming couplers are described for example in US patents 2,600,788, 2,983,608, 3,062,653, 3,127,269, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,834,908 and 3,891,445,in DE patent 1,810,464, in DE patent applications 2,408,665, 2,417,945, 2,418,959 and 2,424,467 and in JP patent applications 20,826/76, 58,922/77, 129,538/74, 74,027/74, 159,336/75, 42,121/77, 74,028/74, 60,233/75, 26,541/76 and 55,122/78.

**[0053]** The most useful yellow-forming couplers are conventional open-chain ketomethylene type couplers. Particular examples of such couplers are benzoyl-acetanilide type and pivaloyl acetanilide type compounds. Yellow-forming couplers that can be used are specifically described in US patents 2,875,057, 3,235,924, 3,265,506, 3,278,658, 3,369,859, 3,408,194, 3,415,652 3,528,322, 3,551,151, 3,682,322, 3,725,072 and 3,891,445, in DE patents 2,219,917, 2,261,361 and 2,414,006, in GB patent 1,425,020, in JP patent 10,783/76 and in JP patent applications 26,133/72, 73,147/73, 102,636/76, 6,341/75, 123,342/75, 130,442/75, 1,827/76, 87,650/75, 82,424/77 and 115,219/77.

**[0054]** Colored couplers can be used which include those described for example in US patents 3,476,560, 2,521,908 and 3,034,892, in JP patent publications 2,016/69, 22,335/63, 11,304/67 and 32,461/69, in JP patent applications 26,034/76 and 42,121/77 and in DE patent application 2,418,959. The light-sensitive silver halide color photographic element may contain high molecular weight color couplers as described for example in US Pat. No. 4,080,211, in EP Pat. Appl. No. 27,284 and in DE Pat. Appl. Nos. 1,297,417, 2,407,569, 3,148,125, 3,217,200, 3,320,079, 3,324,932, 3,331,743, and 3,340,376.

**[0055]** Colored cyan couplers can be selected from those described in US patents 3,934,802; 3,386,301 and 2,434,272, colored magenta couplers can be selected from the colored magenta couplers described in US patents 2,434,272; 3,476,564 and 3,476,560 and in British patent 1,464,361. Colorless couplers can be selected from those described in British patents 861,138; 914,145 and 1,109,963 and in US patent 3,580,722.

**[0056]** Also, couplers providing diffusible colored dyes can be used together with the above mentioned couplers for improving graininess and specific examples of these couplers are magenta couplers described in US Pat. No. 4,366,237 and GB Pat. No. 2,125,570 and yellow, magenta and cyan couplers described in EP Pat. No. 96,873, and in DE Pat. Appl. No. 3,324,533.

**[0057]** Also, among the 2-equivalent couplers are those couplers which carry in the coupling position a group which is released in the color development reaction to give a certain photographic activity, e.g. as development inhibitor or accelerator or bleaching accelerator, either directly or after removal of one or further groups from the group originally released. Examples of such 2-equivalent couplers include the known DIR couplers as well as DAR, FAR and BAR couplers. Typical examples of said couplers are described in DE Pat. Appl. Nos. 2,703,145, 2,855,697, 3,105,026, 3,319,428, 1,800,420, 2,015,867, 2,414,006, 2,842,063, 3,427,235, 3,209,110, and 1,547,640, in GB Pat. Nos. 953,454 and 1,591,641, and in EP Pat. Appl. Nos. 89,843, 117,511, 118,087, 193,389, and 301,477.

**[0058]** Examples of non-color forming DIR coupling compounds which can be used in silver halide color elements include those described in US patents 3,938,996; 3,632,345; 3,639,417; 3,297,445 and 3,928,041; in German patent applications S.N. 2,405,442; 2,523,705; 2,460,202; 2,529,350 and 2,448,063; in Japanese patent applications S.N. 143,538/75 and 147,716/75 and in British patents 1,423,588 and 1,542,705.

**[0059]** In order to introduce the couplers into the silver halide emulsion layer, some conventional methods known to the skilled in the art can be employed. According to US patents 2,322,027, 2,801,170, 2,801,171 and 2,991,177, the couplers can be incorporated into the silver halide emulsion layer by the dispersion technique, which consists of dissolving

the coupler in a water-immiscible high-boiling organic solvent and then dispersing such a solution in a hydrophilic colloidal binder under the form of very small droplets. The preferred colloidal binder is gelatin, even if some other kinds of binders can be used.

**[0060]** Another type of introduction of the couplers into the silver halide emulsion layer consists of the so-called "loaded-latex technique". A detailed description of such technique can be found in BE patents 853,512 and 869,816, in US patents 4,214,047 and 4,199,363 and in EP patent 14,921. It consists of mixing a solution of the couplers in a water-miscible organic solvent with a polymeric latex consisting of water as a continuous phase and of polymeric particles having a mean diameter ranging from 0.02 to 0.2 micrometers as a dispersed phase.

**[0061]** Another useful method is further the Fisher process. According to such a process, couplers having a water-soluble group, such as a carboxyl group, a hydroxy group, a sulfonic group or a sulfonamido group, can be added to the photographic layer for example by dissolving them in an alkaline water solution.

**[0062]** The layers of the photographic elements can be coated on various support bases, such as cellulose ester (e.g., cellulose triacetate), paper, polyester films (e.g., polyethylene terephthalate or naphthalate), and the like, as described in Research Disclosure 308119, XVII, 1989.

**[0063]** The photographic elements, including the silver halide emulsion used in this invention, may be processed to form a visible image upon association of the silver halides with an alkaline aqueous medium in the presence of a developing agent contained in the medium or in the material, as known in the art. The aromatic primary amine color developing agent used in the photographic color developing composition can be any of known compounds of the class of p-phenylendiamine derivatives, widely employed in various color photographic process. Particularly useful color developing agents are the p-phenylendiamine derivatives, especially the N,N-dialkyl-p-phenylene diamine derivatives wherein the alkyl groups or the aromatic nucleus can be substituted or not substituted.

**[0064]** Examples of p-phenilene diamine developers include the salts of: N,N-diethyl-p-phenylendiamine, 2-amino-5-diethylamino-toluene, 4-amino-N-ethyl-N-(a-methanesulphonamidoethyl)-m-toluidine, 4-amino-3-methyl-N-ethyl-N-(a-hydroxy-ethyl)-aniline, 4-amino-3-(a-methylsulfonamidoethyl)-N,N-diethylaniline, 4-amino-N,N-diethyl-3-(N'-methyl-a-methylsulfonamido)-aniline, N-ethyl-N-methoxy -ethyl-3-methyl-p-phenylenediamine and the like, as described, for instance, in US patents No. 2,552,241; 2,556,271; 3,656,950 and 3,658,525.

**[0065]** Examples of commonly used developing agents of the p-phenylene diamine salt type are: 2-amino-5-diethyl-aminotoluene hydrochloride (generally known as CD2 and used in the developing solutions for color positive photographic material), 4-amino-N-ethyl-N-(a-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate (generally known as CD3 and used in the developing solution for photographic papers and color reversal materials) and 4-amino-3-methyl-N-ethyl-N-(b-hydroxy-ethyl)-aniline sulfate (generally known as CD4 and used in the developing solutions for color negative photographic materials).

**[0066]** Said color developing agents are generally used in a quantity from 0.001 to 0.1 moles per liter, preferably from 0045 to 0.04 moles per liter of photographic color developing compositions.

**[0067]** In the case of color photographic materials, the processing comprises at least a color developing bath and, optionally, a prehardening bath, a neutralizing bath, a first (black and white) developing bath, etc. These baths are well known in the art and are described for instance in Research Disclosure 17643, 1978.

**[0068]** After color development, the image-wise developed metallic silver and the remaining silver salts generally must be removed from the photographic element. This is performed in separate bleaching and fixing baths or in a single bath, called blix, which bleaches and fixes the image in a single step. The bleaching bath is a water solution having a pH equal to 5.60 and containing an oxidizing agent, normally a complex salt on an alkali metal or of ammonium and of trivalent iron with an organic acid, e. g. EDTA.Fe.NH4, wherein EDTA is the ethylenediaminotetracetic acid. While processing, this bath is continuously aired to oxidize the divalent iron which forms while bleaching the silver image and regenerated, as known in the art, to maintain the bleach effectiveness. The bad working of these operations may cause the drawback of the loss of cyan density of the dyes.

**[0069]** Further to the above mentioned oxidizing agents, the blix bath contains known fixing agents, such as for example ammonium or alkali metal thiosulfates. Both bleaching and fixing baths can contain other additives, e. g. polyalkyleneoxide derivatives, as described in GB patent 933,008 in order to increase the effectiveness of the bath, or thioethers known as bleach accelerators.

**[0070]** The present invention will be illustrated with reference to the following examples, but it should be understood that these examples do not limit the present invention.

**EXAMPLES.**

Example 1.

**[0071]** Sample 1 (control). A core-shell silver bromoiodide emulsion having a grain size of 1.5 mm was prepared according to the procedure described in US Patent No. 6,258,522.

**[0072]** Prior to starting the chemical digest, the silver halide emulsion concentration was first adjusted to 10.5 % by weight, the pH was corrected to 5.5 and the pAg to 8.4 at a temperature of 40°C. The emulsion was chemically and spectrally sensitized with a conventional sulfur-gold sensitization process while keeping the temperature at 53°C. The following solution concentrations are all expressed in parts per weight in water, unless different solvents are clearly specified. Per each mole of silver, the emulsion was added with 9 cc of heptahydrate zinc sulfate at 0.3 %, 56 cc of green sensitizing dye S-1 at 0.15 % in water and ethyl alcohol, 146 cc of green sensitizing dye S-2 at 0.3 %, 3.3 cc of sodium chloride at 21.5 %, 16.4 cc of benzothiazolium ethyl iodide at 0.2%, a blend of 16.7 cc of sodium para-toluen-sulfinate at 18.96 %, and of 30 cc of sodium para-toluenethiosulfonate at 0.38 % in methyl alcohol, a blend of 16 cc of potassium thiocyanate at 0.3 % and of 17.2 cc of gold chloride at 0.008 % in gold. The digest was performed during 150 minutes at 53°C and the emulsion successively stabilized with 24.8 cc of triazoindolizine at 9.58 % and 40 cc of potassium hexachloropalladate at 0.035 % first to be chilled.

**[0073]** Sample 2 (comparison). The same method for chemically sensitising the Sample 1 emulsion has been used, but the benzothiazolium ethyl iodide compound has been replaced by the same amount of N-allylbenzothiazolium bromide.

**[0074]** Sample 3 (invention). The same method for chemically sensitising the Sample 1 emulsion has been used, but the benzothiazolium ethyl iodide compound has been replaced by 9.4 cc at 0.5 % weight per volume in methyl alcohol of Compound (1) used in the present invention.

**[0075]** A magenta monochrome film having a triacetate support base was obtained from each Samples 1 to 3 by using magenta coupler M-1 and conventional coating formulation. The silver coverage of the magenta layer was 2.65 g $Ag/m^2$. Samples of each film were exposed to a white light source having a color temperature of 5,500 Kelvin. All the exposed samples have been developed after coating in a standard type C41 process as described in British Journal of Photography, July 12, 1974, pp. 597-598. The speeds of the green-sensitive layers, obtained at a density of 0.2 and of 1.0 above minimum density, as well as Dmin and Dmax are reported in the following table 1. The thermal stability (TS) of samples 1 to 3 have been also reported in table 1 by measuring the same sensitometric values (indicated, in this case, by Dmin TS, Dmax TS, Speed 0.1 TS and Speed 1.0 TS) after that the sample emulsions have been maintained at 45°C for a coating waiting time of 24 hours.

Table 1

| | Dmin | Dmin TS | Dmax | Dmax TS | Speed 0.2 | Speed 0.2 TS | Speed 1.0 | Speed 1.0 TS |
|---|---|---|---|---|---|---|---|---|
| Sample 1 (Control) | 0.10 | 0.13 | 1.80 | 1.94 | 2.46 | 2.32 | 1.76 | 1.69 |
| Sample 2 (Comparison) | 0.09 | 0.12 | 1.61 | 1.71 | 2.52 | 2.41 | 1.79 | 1.70 |
| Sample 3 (Invention) | 0.10 | 0.11 | 1.85 | 2.08 | 2.46 | 2.43 | 1.81 | 1.84 |

**[0076]** The data of Table 1 clearly show the superior overall characteristics of the silver halide emulsion (Sample 3) chemically sensitized by the method of the present invention. In fact, not only all the typical sensitometric values, such as Dmin, Dmax and Speeds associated to Sample 3 are good, but they also show a good thermal stability upon storage, as clearly shown by the data related to Dmin TS, Dmax TS and Speeds TS. On the contrary, the data of comparison Samples 1 and 2, obtained by emulsions chemically sensitized by a process not belonging to the present invention, show a decrease in the sensitometric values related to thermal stabilty.

Example 2.

**[0077]** Sample 4 (comparison). The same method for chemically sensitising the Sample 1 emulsion has been used.

**[0078]** Sample 5 (invention). The same method for chemically sensitising the Sample 1 emulsion has been used, but the benzothiazolium ethyl iodide compound has been replaced by 9.4 cc at 0.5 % weight per volume in methyl alcohol of Compound (8) used in the present invention.

**[0079]** A magenta monochrome film having a triacetate support base was obtained from each Samples 4 and 5 as described in Example 1; samples of each film were exposed, developed and evaluated as in Example 1. Table 2 reports the same sensitometric data of Table 1 related to Samples 4 and 5.

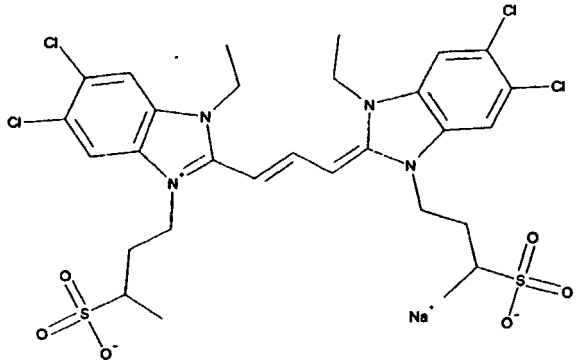
Table 2

| | Dmin | Dmin TS | Dmax | Dmax TS | Speed 0.2 | Speed 0.2 TS | Speed 1.0 | Speed 1.0 TS |
|---|---|---|---|---|---|---|---|---|
| Sample 4 (Control) | 0.13 | 0.17 | 1.65 | 1.77 | 2.62 | 2.53 | 1.94 | 1.89 |
| Sample 5 (Invention) | 0.11 | 0.13 | 1.71 | 1.98 | 2.53 | 2.52 | 1.90 | 1.92 |

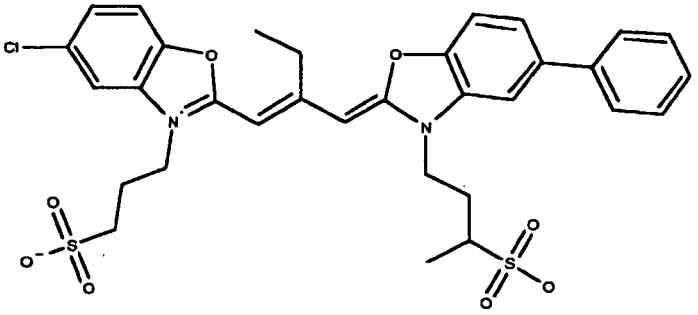
**[0080]** Also the data of Table 2 clearly show the superior good thermal stability upon storage characteristics of the silver halide emulsion (Sample 5) chemically sensitized by the method of the present invention compared with Sample 4, obtained by emulsions chemically sensitized by a process not belonging to the present invention.

**[0081]** Formulas of compounds used in the present invention will be presented below.

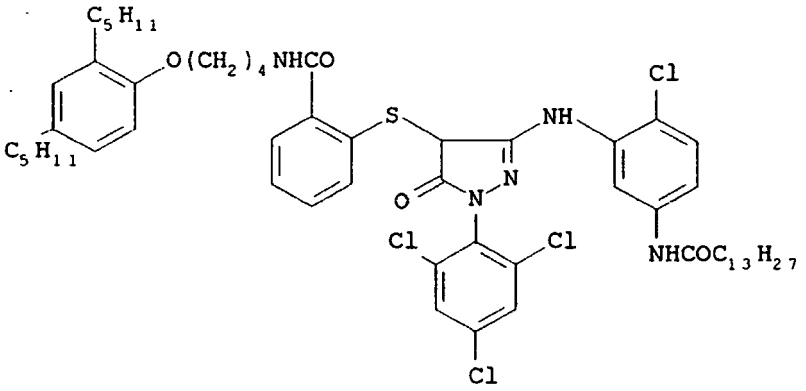
Green Sensitizing Dye S-1




Green Sensitizing Dye S-2

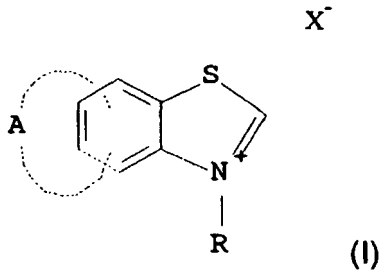


Magenta Coupler M-1



## Claims

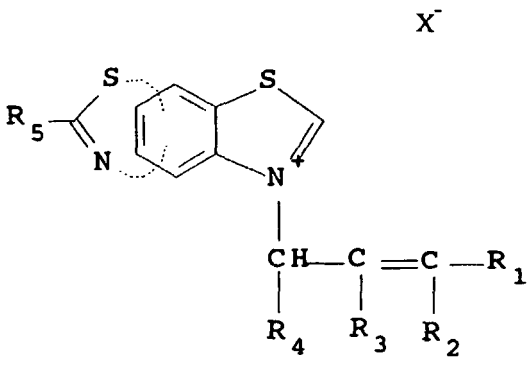
1. Process for chemically sensitizing a silver halide photographic emulsion including the addition to said emulsion, during the chemical sensitization, of a benzo-bis-thiazole quaternary salt represented by the general formula (I):



(I)

wherein R is an alkyl, an alkenyl or an alkinyl group having from 1 to 5 carbon atoms, A represents the atoms necessary to complete a benzo-bis-thiazole nucleus and $X^-$ is an anion.

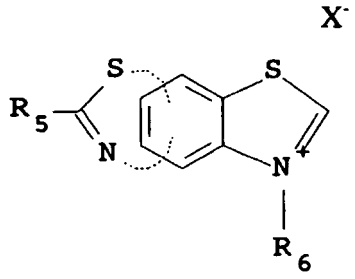
2. Process for chemically sensitizing a silver halide photographic emulsion according to claim 1, wherein the benzo-bis-thiazole quaternary salt is represented by the general formula (II):



(II)

wherein $R_1$, $R_2$, $R_3$, $R_4$ and $R_5$ each represents a hydrogen atom or a low alkyl group having from 1 to 5 carbon atoms and $X^-$ is an anion.

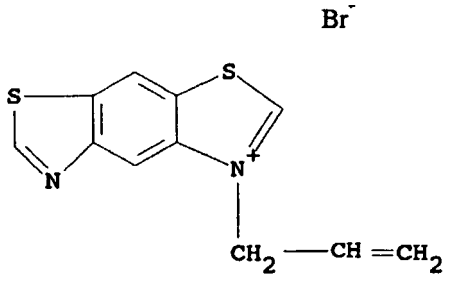
3. Process for chemically sensitizing a silver halide photographic emulsion according to claim 1, wherein the benzo-bis-thiazole quaternary salt is represented by the general formula (III):



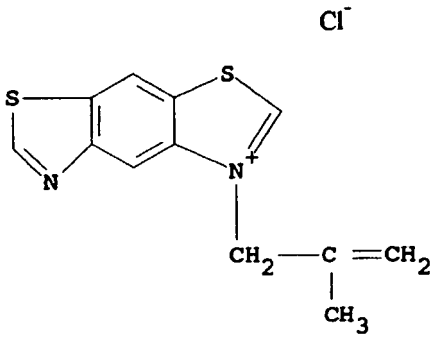
(III)

wherein $R_5$ is hydrogen atom or a low alkyl group having 1 to 5 carbon atoms, $R_6$ is a low alkyl group having 1 to 3 carbon atoms, and $X^-$ is an anion.

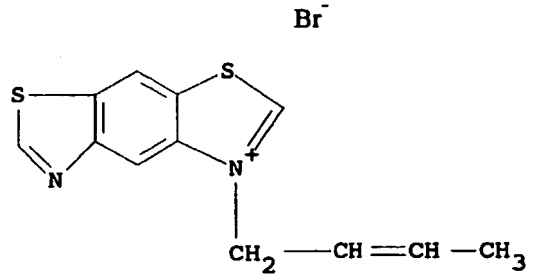
4. Process for chemically sensitizing a silver halide photographic emulsion according to claim 1, wherein the benzo-bis-thiazole quaternary salt is one of the following compounds:



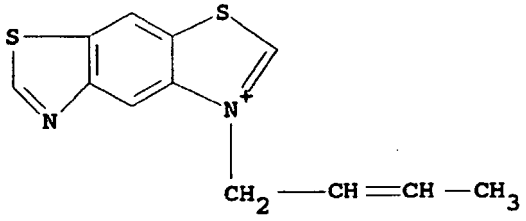
(1)



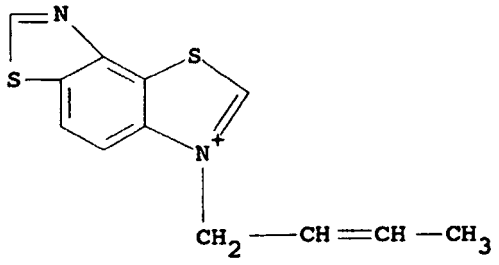
(2)



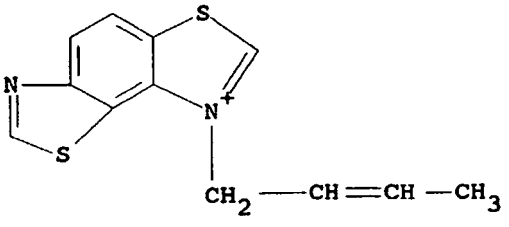
(3)



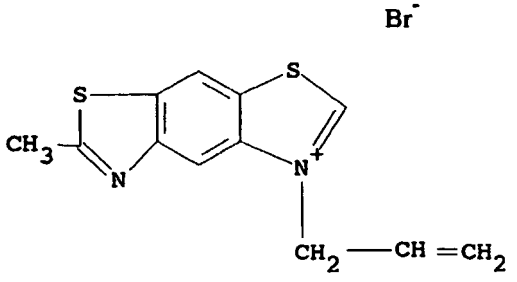
(4)



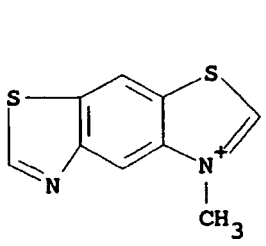
(5)



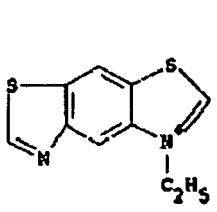
(6)



(7)



(8)



(9)

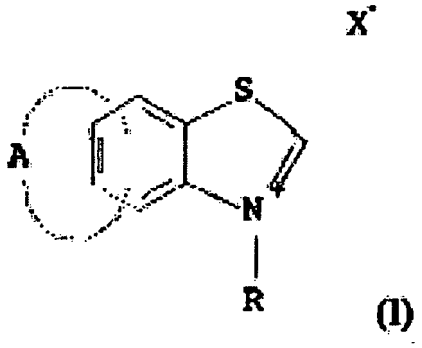
5. Process for chemically sensitizing a silver halide photographic emulsion according to daim 1 further including the addition of a sulfur sensitizer to said emulsion.

6. Process for chemically sensitizing a silver halide photographic emulsion according to claim 5, wherein said sulfur sensitizer is a thiosulfonate salts, sodium thiosulfate, allylthiocyanate, allylthiourea, thiosulfinic acid, sulfonic add, allylthiocarbamide, thiourea or cystine.

7. Process for chemically sensitizing a silver halide photographic emulsion according to claim 5, wherein said sulfur sensitizer is para-toluenethiosulfonate salts.

8. Process for chemically sensitizing a silver halide photographic emulsion according to claim 5, wherein said sulfur sensitizer is added after the addition of the benzo-bis-thiazole quaternary salt.

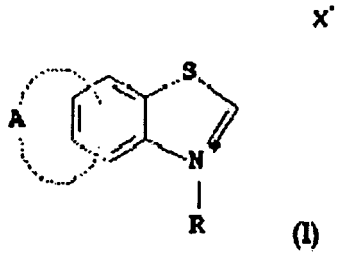
9. Chemically sensitized silver halide light green-sensitive emulsion containing a benzo-bis-thiazole quaternary salt represented by the general formula (I):



(I)

wherein R is an alkyl or an alkinyl group having from 1 to 5 carbon atoms, A represents the atoms necessary to complete a benzo-bis-thiazole nucleus and X<-> is an anion.

**10.** Silver halide light-sensitive material comprising a support base carrying at least one silver halide blue-sensitive emulsion layer associated with a yellow dye-forming coupler, at least one silver halide green-sensitive emulsion layer associated with a magenta dye-forming coupler and at least one silver halide red-sensitive silver halide emulsion layer associated with a cyan dye-forming coupler, wherein at least one silver halide green-sensitive emulsion layer contains a chemically sensitized silver halide green-sensitive emulsion comprising a benzo-bis-thiazole quaternary salt represented by the general formula (I):

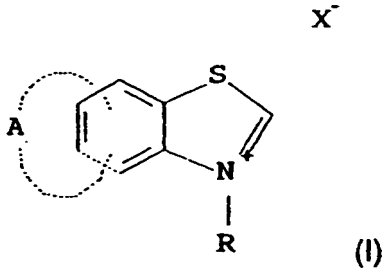


(I)

wherein R is an alkyl or an alkinyl group having from 1 to 5 carbon atoms, A represents the atoms necessary to complete a benzo-bis-thiazole nucleus and X<-> is an anion.

## Patentansprüche

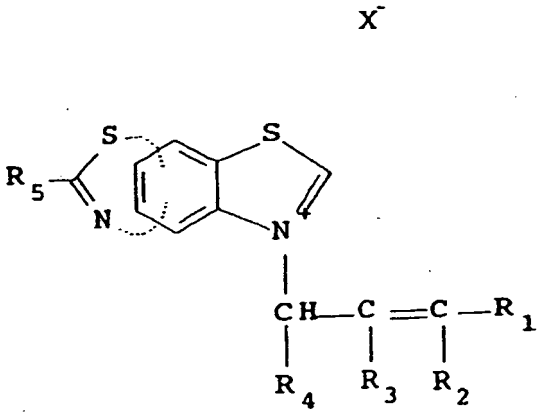
**1.** Verfahren zum chemischen Sensibilisieren einer photographischen Silberhalogenid-Emulsion, einschließlich der Zugabe eines Quartärsalzes von Benzo-bis-thiazol zu der Emulsion, während der chemischen Sensibilisierung, dargestellt durch die allgemeine Formel (I):



(I)

worin R eine Alkyl-, eine Alkenyl- oder eine Alkinylgruppe ist, die 1 bis 5 Kohlenstoffatome hat, A die Atome darstellt, die notwendig sind, um einen Benzo-bis-thiazol-Ring zu vervollständigen, und $X^-$ ein Anion ist.

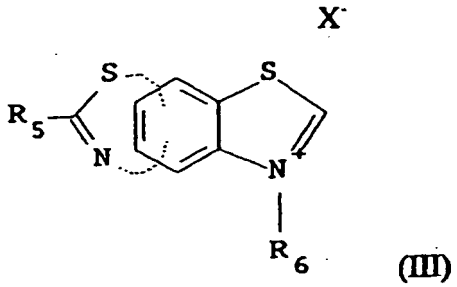
**2.** Verfahren zum chemischen Sensibilisieren einer photographischen Silberhalogenid-Emulsion nach Anspruch 1, worin das Quartärsalz von Benzo-bis-thiazol durch die allgemeine Formel (II) dargestellt wird:



(II)

worin $R_1$, $R_2$, $R_3$, $R_4$ und $R_5$ jeweils ein Wasserstoffatom oder eine niedrige Alkylgruppe darstellt, die 1 bis 5 Kohlenstoffatome hat, und $X^-$ ein Anion ist.

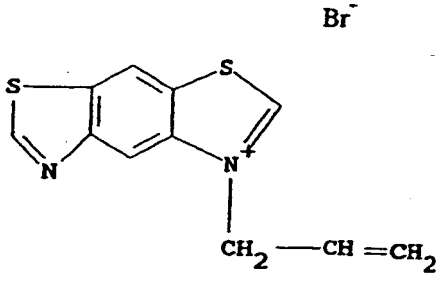
**3.** Verfahren zum chemischen Sensibilisieren einer photographischen Silberhalogenid-Emulsion nach Anspruch 1, worin das Quartärsalz von Benzo-bis-thiazol durch die allgemeine Formel (III) dargestellt wird:



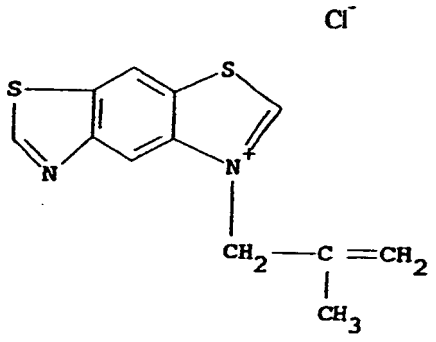
(III)

worin $R_5$ ein Wasserstoffatom oder eine niedrige Alkylgruppe ist, die 1 bis 5 Kohlenstoffatome hat, $R_6$ eine niedrige Alkylgruppe ist, die 1 bis 3 Kohlenstoffatome hat, und $X^-$ eine Anion ist.

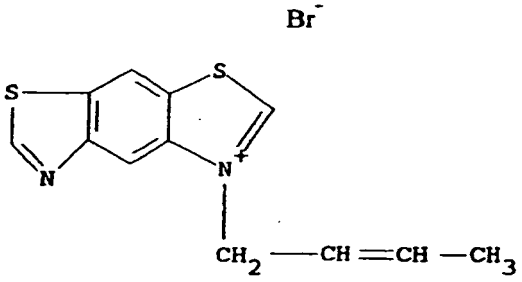
**4.** Verfahren zum chemischen Sensibilisieren einer photographischen Silberhalogenid-Emulsion nach Anspruch 1, worin das Quartärsalz von Benzo-bis-thiazol aus den folgenden Komponenten besteht:



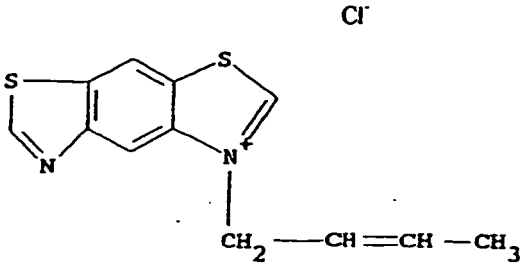
(I)



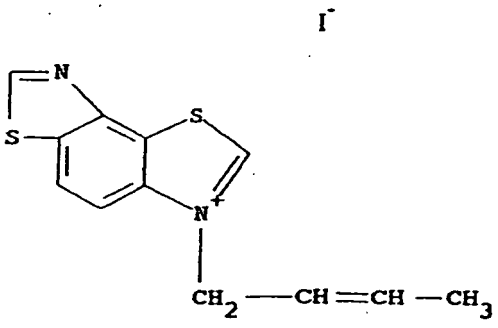
(2)



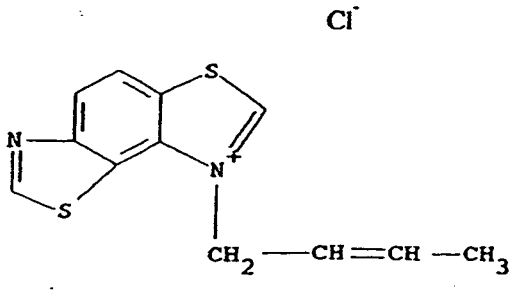
(3)



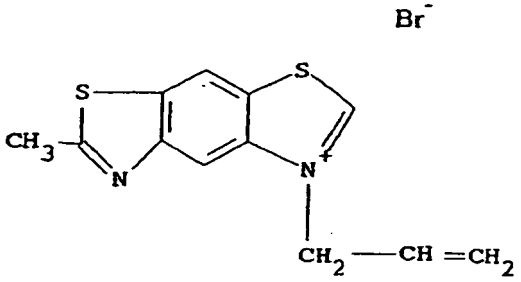
(4)



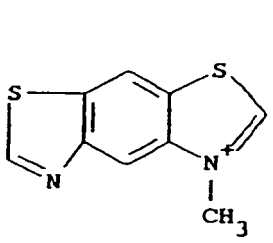
(5)



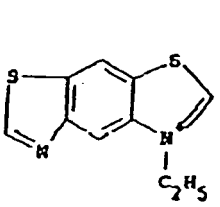
(6)



(7)



(8)



(9)

**5.** Verfahren zum chemischen Sensibilisieren einer photographischen Silberhalogenid-Emulsion nach Anspruch 1, weiterhin einschließend die Zugabe eines Schwefel-Sensibilisators zu der Emulsion.

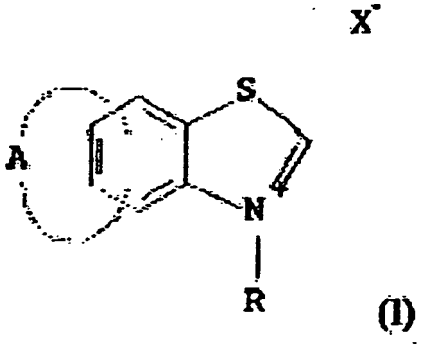
**6.** Verfahren zum chemischen Sensibilisieren einer photographischen Silberhalogenid-Emulsion nach Anspruch 5, worin der Schwefel-Sensibilisator ein Thiosulfonatsalz, Natriumthiosulfat, Allylthiocyanat, Allylthioharnstoff, Thiosulfinsäure, Sulfonsäure, Allylthiocarbamid, Thioharnstoff oder Cystin ist.

**7.** Verfahren zum chemischen Sensibilisieren einer photographischen Silberhalogenid-Emulsion nach Anspruch 5, worin der Schwefel-Sensibilisator para-Toluolthiosulfonatsalze ist.

**8.** Verfahren zum chemischen Sensibilisieren einer photographischen Silberhalogenid-Emulsion nach Anspruch 5,

worin der Schwefel-Sensibilisator nach Zugabe des Quartärsalzes von Benzo-bis-thiazol hinzugefügt wird.

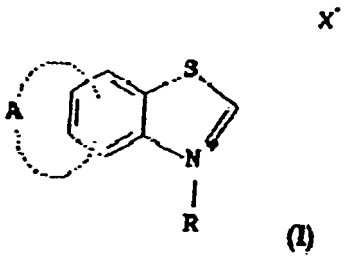
**9.** Chemisch sensibilisierte hellgrün-sensitive Silberhalogenid-Emulsion, enthaltend ein Quartärsalz von Benzo-bis-thiazol, das durch die allgemeine Formel (I) dargestellt wird:




(I)

worin R eine Alkyl- oder eine Alkinylgruppe ist, die 1 bis 5 Kohlenstoffatome hat, A die Atome darstellt, die notwendig sind, um einen Benzo-bis-thiazol-Ring zu vervollständigen, und X <-> ein Anion ist.

**10.** Licht-sensitives Silberhalogenid-Material, umfassend eine Trägerbasis, die mindestens eine blau-sensitive Silberhalogenid-Emulsionsschicht trägt, die mit einem gelben farbstoffbildenden Kuppler verbunden ist, mindestens eine grün-sensitive Silberhalogenid-Emulsionsschicht trägt, die mit einem Magenta-farbstoffbildenden Kuppler verbunden ist, und mindestens eine Silberhalogenid-rot-sensitive Silberhalogenid-Emulsionsschicht trägt, die mit einem Cyan-farbstoffbildenden Kuppler verbunden ist, worin mindestens eine grün-sensitive Silberhalogenid-Emulsionsschicht eine chemisch sensibilisierte grün-sensitive Silberhalogenid-Emulsion enthält, die ein Quartärsalz von Benzo-bis-thiazol umfasst, das durch die allgemeine Formel (I) dargestellt wird:

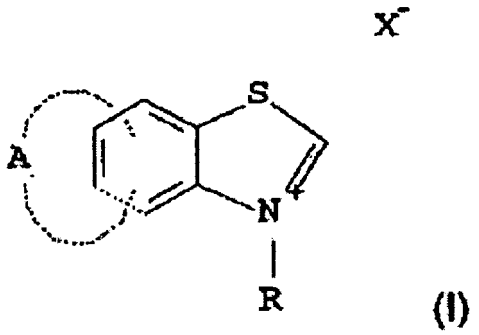



(I)

worin R eine Alkyl- oder Alkinylgruppe ist, die 1 bis 5 Kohlenstoffatome hat, A die Atome darstellt, die notwendig sind, um einen Benzo-bis-thiazol-Ring zu vervollständigen, und X <-> ein Anion ist.

**Revendications**

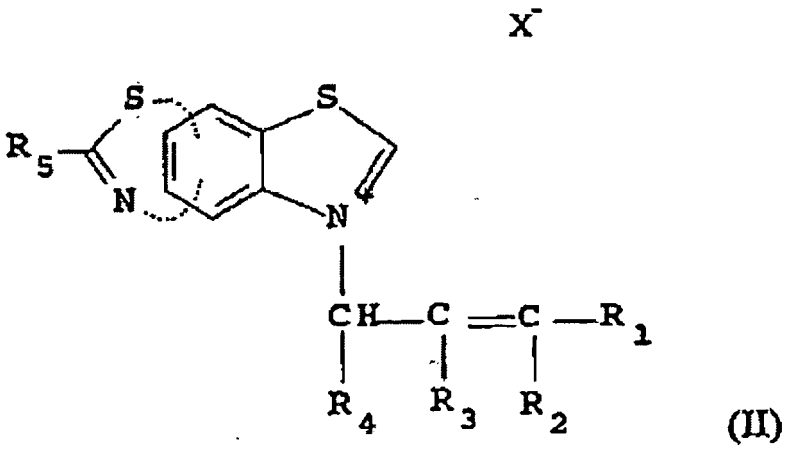
**1.** Procédé pour sensibiliser chimiquement une émulsion photographique à l'halogénure d'argent comprenant l'addition à cette émulsion pendant la sensibilisation chimique d'un sel quaternaire de benzo-bis-thiazole représenté par la formule (I) ;



(I)

dans laquelle R est un groupe (I) alkyle, alcènyle ou alcinyle ayant entre 1 et 5 atomes de carbone, A représente les atomes nécessaires pour compléter un noyau de benzo-bis-thiazole et $X^-$ est un anion.

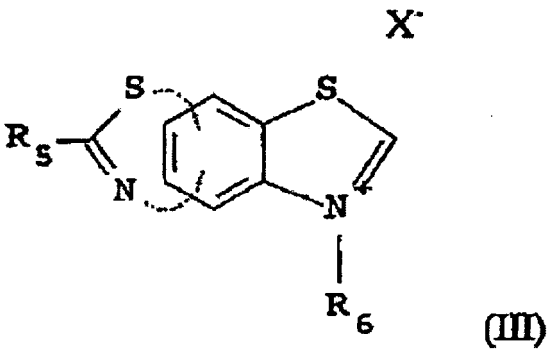
**2.** Procédé pour sensibiliser chimiquement une émulsion photographique à l'halogénure d'argent selon la revendication 1, dans laquelle le sel quaternaire de benzo-bis-thiazole est représenté par la formule générale (II) :



(II)

dans laquelle $R_1$, $R_2$, $R_3$, $R_4$ et $R_5$ représentent chacun un atome d'hydrogène ou un groupe alkyle inférieur ayant entre 1 et 5 atomes de carbone et $X^-$ est un anion.

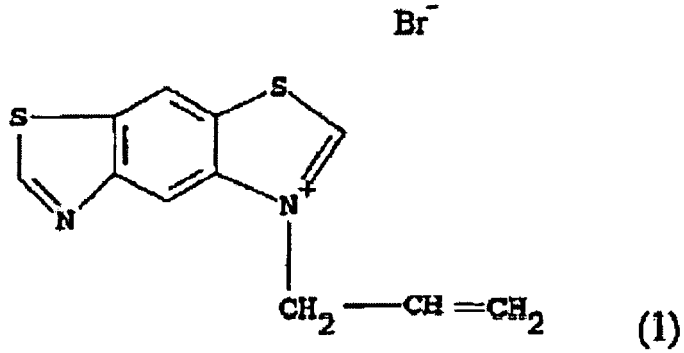
**3.** Procédé pour sensibiliser chimiquement une émulsion photographique à l'halogénure d'argent selon la revendication 1, dans laquelle le sel quaternaire de benzo-bis-thiazole est représenté par la formule générale (III) :



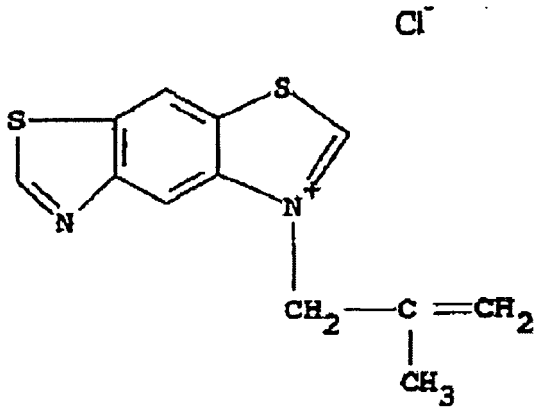
(III)

dans laquelle $R_5$ est un atome d'hydrogène ou un groupe alkyle inférieur ayant entre 1 et 3 atomes de carbone et $X^-$ est un anion.

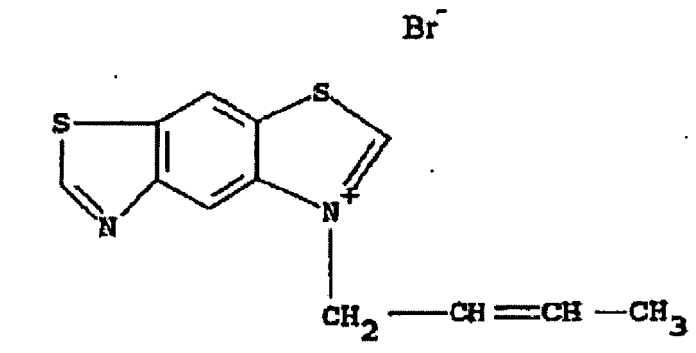
**4.** Procédé pour sensibiliser chimiquement une émulsion photographique à l'halogénure d'argent selon la revendication 1, dans laquelle le sel quaternaire de benzo-bis-thiazole est l'un des composés suivants :



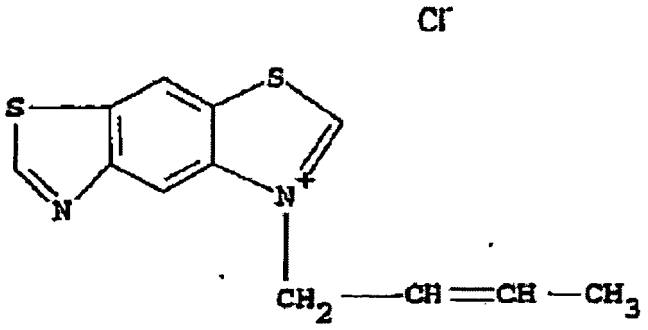
(1)



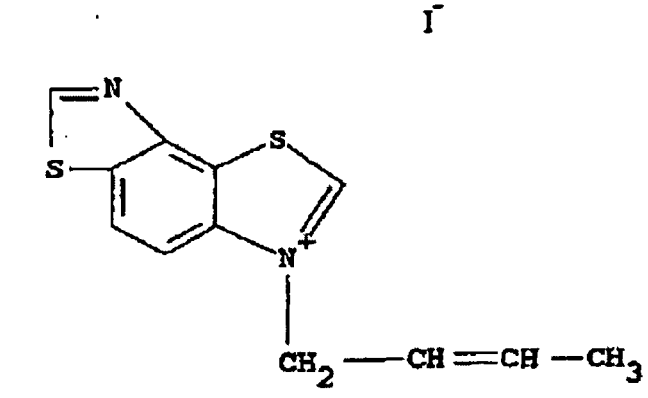
(2)



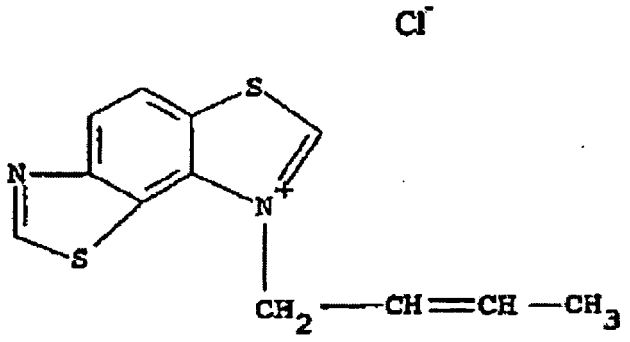
(3)



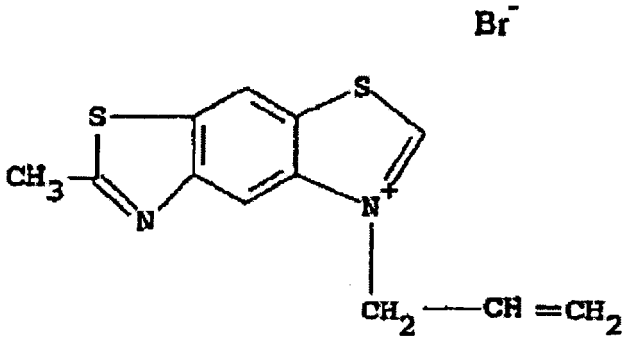
(4)



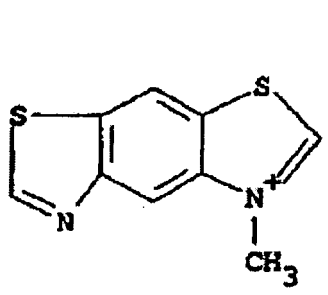
(5)



(6)



(7)



(8)

**5.** Procédé pour sensibiliser chimiquement une émulsion photographique à l'halogénure d'argent selon la revendication 1 comprenant en outre l'addition à l'émulsion d'un agent de sensibilisation à base de soufre.

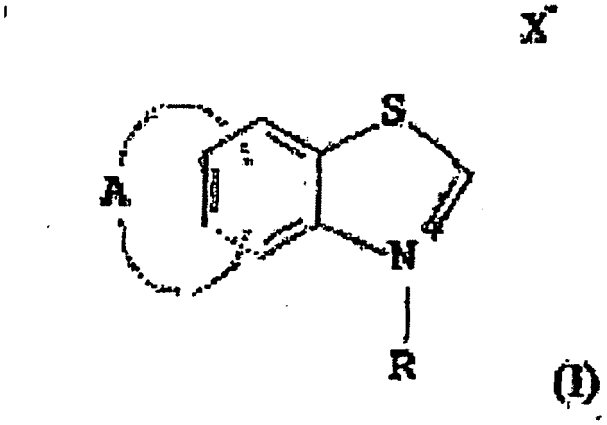
**6.** Procédé pour sensibiliser chimiquement une émulsion photographique à l'halogénure d'argent selon la revendication 5, dans lequel ledit agent de sensibilisation à base de soufre et un sel de thiosulfonate, un thiosulfate de sodium, un allylthiocyanate, de l'allylthiourée, de l'acide thiosulfinique, de l'acide sulfonique, de l'allythiocarbamide, de la thiourée ou de la cystine.

**7.** Procédé pour sensibiliser chimiquement une émulsion photographique à l'halogénure d'argent selon la revendication

5, dans lequel ledit agent de sensibilisation à base de soufre est un sel de para-toluènethiosulfonate.

**8.** Procédé pour sensibiliser chimiquement une émulsion photographique à l'halogénure d'argent selon la revendication 5, dans lequel ledit agent de sensibilisation à base de soufre est ajouté après l'addition du sel quaternaire de benzo-bis-thiazole.

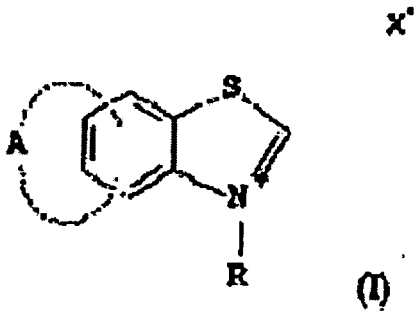
**9.** Emulsion sensibilisée chimiquement à l'halogénure d'argent sensible à la lumière verte contenant un sel quaternaire de benzo-bis-thiazole représenté par la formule générale (I) :




(I)

dans laquelle R est un groupe alkyl ou alcinyle ayant entre 1 et 5 atomes de carbone, A représente les atomes nécessaires pour compléter un noyau de benzo-bis-thiazole et $X^-$ est un anion.

**10.** Matériau sensible à la lumière à base d'halogénure d'argent comprenant un support de base portant au moins une couche d'émulsion à l'halogénure d'argent sensible au bleu associée à un coupleur formant une teinture jaune, au moins une couche d'émulsion à l'halogénure d'argent sensible au vert associée à un coupleur formant une teinture magenta et au moins une couche d'émulsion à l'halogénure d'argent sensible au rouge associée à un coupleur formant une teinture cyan, dans lequel au moins l'une des couches d'émulsions à l'halogénure d'argent sensible au vert contient une émulsion à l'halogénure d'argent sensibilisée chimiquement, sensible au vert comprenant un sel quaternaire de benzo-bis-thiazole représenté par la formule générale (I)




(I)

dans laquelle R est un groupe alkyl ou alcinyle ayant entre 1 et 5 atomes de carbone, A représente les atomes nécessaires pour compléter un noyau de benzo-bis-thiazole et $X^-$ est un anion.