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(54) Sensitization process of silver halide photographic emulsion

(57) A process for chemically sensitizing a silver halide photographic emulsion comprising the steps of:
(a) adding to the silver halide photographic emulsion a noble metal and at least one metal selected from the group consisting of Group II metals, Group VIII metals, and Group IIB metals, and thereafter (b) adding to the resulting silver halide photographic emulsion a sulfur sensitizer. A silver halide solvent and/or a stabilizer are preferably added at any time before the addition of the sulfur sensitizer. A radiographic element comprising the silver halide photographic emulsion obtained with the above mentioned chemical sensitization process is also claimed.

Description**FIELD OF THE INVENTION**

5 The present invention relates to a sensitization process of a silver halide photographic emulsion. More particularly, the present invention relates to a chemical sensitization process employing a noble metal, a metal chosen from Groups II, VIII, and IIB of the periodic table and a sulfur chemical sensitizer. The present invention also relates to a radio-graphic element comprising the silver halide photographic emulsion obtained with the above mentioned chemical sensitization process.

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BACKGROUND OF THE INVENTION

Silver halide emulsions are usually prepared by precipitating silver halide (silver bromide, silver iodide, silver chloride or mixture thereof) in the presence of a hydrophilic colloid (normally gelatin).

15 Afterwards, the silver halide emulsions have to be subjected to a sensitization process for increasing their sensitivity to light. The sensitization process mainly involves spectral sensitization and chemical sensitization.

Spectral sensitization comprises the addition of spectral sensitizing dyes which can be adsorbed on the silver halide grain surface in order to make the emulsion sensitive to visible or infrared radiation.

Chemical sensitization comprises the addition of various chemical substances to obtain a prescribed value of sensitivity and contrast. Typical methods for chemical sensitizing a silver halide photographic emulsion include sulfur sensitization, noble metal sensitization, and reduction sensitization. It is also common in the art to have combination methods, such as sulfur-noble metal sensitization, reduction-noble metal sensitization, and the like.

20 A number of patents and patent applications, as well as literature references discloses specific methods to improve chemical sensitization. Research Disclosure, September 1994, Item 36544, Paragraph IV, pp. 510-511, gives a wide array of references for each of the above-mentioned methods.

25 In recent years, there has been a strong demand for high sensitivity, low graininess and low fog in a silver halide photographic element as well as for rapid processing in which development is expedited. Various improvements in the above sensitizing methods have been made.

30 Additionally, a wide range of metals have been used as doping agents during emulsion making of silver halide emulsions in order to modify grain structure and properties. A general review of the use of these doping agents can be found in Research Disclosure, September 1994, Item 36544, Paragraph II.D.3, pp. 504-505.

Some recent patents and patent applications teach the use of some metals during chemical sensitization alone or in combination with the above mentioned conventional method.

35 EP 467,106 discloses a silver halide photographic element chemically sensitized by gold and sulfur compounds and further by a mercury compound.

JP 4/009,034 discloses silver halide photographic element chemically sensitized by gold in the presence of an iridium or a platinum complex salt.

JP 4/009,837 discloses silver halide photographic element chemically sensitized by reduction sensitization and further by a palladium compound.

40 EP 476,345 discloses silver halide photographic element chemically sensitized in the presence of a noble metal, a sulfur sensitizer, a selenium compound and a silver halide solvent.

JP 4/051,232 discloses silver halide photographic element chemically sensitized in the presence of a gold compound, an iridium compound, and a Group VIII metal compound.

45 JP 5/045,768 discloses silver halide photographic element chemically sensitized in the presence of a tellurium organic compound and a gold compound. JP 5/053,234 further discloses the possibility of an additional reduction sensitization.

JP 5/045,769 discloses silver halide photographic element chemically sensitized in the presence of tellurium, sulfur and noble metal organic compounds.

50 JP 4/335640, 5/027,360, 5/027,388, EP 563,708 and EP 638,840 disclose silver halide photographic element chemically sensitized in the presence of selenium, gold and sulfur sensitizer.

EP 568,092 discloses silver halide photographic element chemically sensitized in the presence of a heavy metal and a thiourea compound.

JP 6/51,418 discloses silver halide photographic element chemically sensitized in the presence of a mercuric chloride organic derivative, sodium thiocyanate, sodium thiosulfate, and potassium chloroaurate.

55 However, none of the above patents and patent applications discloses or suggests the present invention as will be described hereinbelow.

SUMMARY OF THE INVENTION

The present invention provides a process for chemically sensitizing a silver halide photographic emulsion comprising the following steps:

5 (a) adding to a silver halide photographic emulsion a noble metal and at least one metal selected from the group consisting of Group II metals, Group VIII metals, and Group IIB metals and thereafter,
 (b) adding to the resulting silver halide photographic emulsion a sulfur sensitizer.

10 In a preferred embodiment of the present invention, a silver halide solvent and/or a stabilizer can be added at any time before the addition of the sulfur sensitizer.

Another aspect of the present invention relates to a radiographic element comprising the silver halide photographic emulsion obtained with the above mentioned chemical sensitization process.

15 Other aspects, advantages, and benefits of the present invention will be apparent from the detailed description, examples, and claims.

DETAILED DESCRIPTION OF THE INVENTION

The manufacturing process of silver halide elements usually comprises an emulsion-making step, a chemical and 20 optical sensitization step, and a coating step.

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.

25 Silver halide emulsions can be prepared using a single-jet method, a double-jet method, or a combination of these methods and can be ripened using, for instance, an ammonia method, a neutralization method, or an acid method. Parameters which may be adjusted to control grain growth include pH, pAg, temperature, shape and size of reaction vessel, and the reaction method (e.g., accelerated or constant flow rate precipitation, interrupted precipitation, ultrafiltration during precipitation, reverse mixing processes and combinations thereof). A silver halide solvent, such as ammonia, thioethers, thioureas, etc., may be used, if desired, for controlling grain size, grain structure, particle size distribution 30 of the grains, and the grain-growth rate. 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, Chimie et Physique Photographique, P. Glafkides, Paul Montel (1967), Photographic Emulsion Chemistry, G. F. Duffin, The Focal Press (1966), Making and Coating Photographic Emulsions, V. L. Zelikman, The Focal Press (1966), in U.S. Pat. 35 Nos. 2,222,264; 2,592,250; 3,650,757; 3,917,485; 3,790,387; 3,716,276; and 3,979,213; Research Disclosure, Sept. 1994, Item 36544 "Photographic Silver Halide Emulsions, Preparations, Addenda, Systems and Processing."

40 In the preparation of the silver halide emulsion to be subjected to the chemical sensitization process of the present invention, commonly employed halogen compositions of the silver halide grains can be used. Typical 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 for tabular silver halide grains 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.

45 The grains of these silver halide emulsions may be coarse or fine, and the grain size distribution of them may be narrow or extensive. Further, the silver halide grains may be regular grains having a regular crystal structure such as cube, octahedron, and tetradecahedron, or the spherical or irregular crystal structure, or those having crystal defects such as twin planes, or those having a tabular form, or combination thereof. Furthermore, the grain structure of the silver halides may be uniform from the interior to exterior thereof, or be multilayer. In a simple embodiment, the grains may 50 comprise a core and a shell, which may have different halide compositions and/or may have undergone different modifications such as the addition of doping agents. Besides having a differently composed core and shell, the silver halide grains may also comprise different phases in-between. Furthermore, the silver halides may be of such a type as allows a latent image to be formed mainly on the surface thereof or of such type as allows it to be formed inside the grains thereof.

In a preferred embodiment, tabular silver halide emulsions are employed in the process of the present invention.

55 Tabular silver halide emulsions are characterized by the average diameter:thickness ratio of silver halide grains (often referred to in the art as aspect ratio). Tabular silver halide having an aspect ratio of at least 2:1, preferably, 2:1 to 20:1, more preferably, 2:1 to 14:1, and most preferably, 2:1 to 8:1 are used in the process of the present invention. Average diameters of the tabular silver halide grains suitable for use in the process of the present invention range from about

0.3 to about 5 μm , preferably, from about 0.5 to about 3 μm , more preferably, from about 0.8 to about 1.5 μm . The tabular silver halide grains suitable for use in the process of the present invention have a thickness of less than 0.4 μm , preferably, less than 0.3 μm , and more preferably, within 0.1 to 0.3 μm . The projected area of the tabular silver halide grains accounts for at least 50%, preferably, at least 80%, and more preferably, at least 90% of the projected area of all the silver halide grains of the emulsion.

The tabular silver halide grain dimensions and 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 method used, the average diameter:thickness ratios obtained do not greatly differ.

Silver halide emulsions containing tabular silver halide grains can be prepared by various processes known to those of ordinary skill in the art for the preparation of photographic elements.

Preparation of silver halide emulsions containing tabular silver halide grains is described, for example, in de Cugnac and Chateau, "Evolution of the Morphology of Silver Bromide Crystals During Physical Ripening", Science and Industries Photographiques, Vol. 33, No.2 (1962), pp.121-125, in Gutoff, "Nucleation and Growth Rates During the Precipitation of Silver Halide Photographic Emulsions", Photographic Science and Engineering, Vol. 14, No. 4 (1970), pp. 248-257, in Berry et al., "Effects of Environment on the Growth of Silver Bromide Microcrystals", Vol.5, No.6 (1961), pp. 332-336, in Research Disclosure, Sept. 1994, Item 36544 "Photographic Silver Halide Emulsions, Preparations, Addenda, Systems and Processing", in U.S. Pat. Nos. 4,063,951; 4,067,739; 4,184,878; 4,434,226; 4,414,310; 4,386,156; and 4,414,306; and in EP Pat. Appln. No. 263,508.

At the end of the tabular silver halide grain formation, water soluble salts are removed from the emulsion by procedures known in the art. Suitable washing processes are those wherein the dispersing medium and soluble salts dissolved therein can be removed from the silver halide emulsion on a continuous basis, such as, for example, a combination of dialysis or electrodialysis for the removal of soluble salts or a combination of osmosis or reverse osmosis for the removal of the dispersing medium.

Among the known techniques for removing the dispersing medium and soluble salts while retaining silver halide grains in the remaining dispersion, ultrafiltration is a particularly advantageous washing processes for the practice of this process. Typically, an ultrafiltration unit comprising membranes of inert, non-ionic polymers is used as a washing process. Since silver halide grains are large in comparison with the dispersing medium and the soluble salts or ions, silver halide grains are retained by the membranes while the dispersing medium and the soluble salts dissolved therein are removed.

In the process of the present invention, the chemical sensitization of the above described silver halide emulsion is performed by first adding a noble metal compound and at least one metal selected from the group consisting of Group IIa metals, Group VIII metals, and Group IIB metals, and thereafter adding a sulfur sensitizer.

Noble metal compounds useful in the practice of the present invention include gold derivatives (such as, for example, potassium chloroaurate, gold chloride, and the like), platinum derivatives (such as platinum chloride), and palladium derivatives such as sodium hexachloropalladate). Gold derivatives are preferably used in the process of the present invention. Specific examples of gold derivatives include chloroauric acid, potassium chloroaurate, auric trichloride, sodium aurithiosulfate, potassium aurithiocyanate, potassium iodoaurate, tetracyanoauric acid, 2-aurosulfobenzothiazole methochloride and ammonium aurothiocyanate. The amount of noble metal can range from 1×10^{-9} to 1×10^{-3} moles per mole of Ag, preferably, from 1×10^{-7} to 1×10^{-4} moles per mole of Ag.

Representative examples of Group II metals useful in the process of the present invention are Mg, Ca, and Sr; representative examples of Group VIII metals useful in the process of the present invention are Fe, Co, Ni, Rh, Ir, Pd, and Pt; and representative examples of Group IIB metals useful in the process of the present invention are Zn, Cd, and Hg. In a preferred embodiment of the present invention, the metal is selected from the group consisting of Mg, Ca, Rh, Ir, Pd, Cu, Zn, Cd, and Hg. Preferred metals include metals selected from the group consisting of Mg, Pd, Zn, and Hg. The amount of the additional metal(s) can range from 1×10^{-9} to 1×10^{-3} moles per mole of Ag, preferably, from 1×10^{-7} to 1×10^{-4} moles per mole of Ag.

The order of addition of the noble metal and the at least one additional metal is not particularly relevant in the practice of the present invention. All metals can be mixed together and added contemporaneously to the silver halide emulsion, or they can be added following a step-by-step procedure. They can be added in solid form or in solution, preferably, in a water solution.

After the metal additions described above, a sulfur chemical sensitizer is added in the process of the present invention in an amount of from 1×10^{-6} to 1×10^{-1} grams per mole of silver, preferably, from 1×10^{-4} to 1×10^{-2} grams per mole of

silver.

Suitable sulfur sensitizers include thiosulfates, such as ammonium thiosulfate, thioureas, such as allylthiocarbamidourea, isothiocyanates, such as allyl isothiocyanate, sulfur-containing aminoacids, such as cystine, thiosulfonates, such as p-toluene thiosulfonates and rhodanines. Thiosulfates, such as, for example, sodium thiosulfate, potassium thiosulfate, and ammonium thiosulfate are the most preferred sulfur sensitizers employed in the process of the present invention.

In a preferred embodiment of the present invention, a silver halide solvent is added at any time before the addition of the sulfur sensitizer, preferably before or together with the metal additions. The term "silver halide solvent" as employed herein means a solubilizing agent for silver halide. It is particularly preferred that a silver halide solvent is present before the addition of the noble metal and the at least one additional metal, but the silver halide solvent can be added together with the metal additions. Any kind of silver halide solvent can be used in the practice of the present invention, but silver halide solvents also acting as complexing agents for the metals are preferred. Useful examples of silver halide solvents include ammonia, thiocyanate derivatives and salts thereof, thioether derivatives, and thiourea derivatives. Thiocyanate derivatives and salts thereof are more preferably used, and most preferably, sodium thiocyanate and potassium thiocyanate. The amount of silver halide solvent can range from 0.01 to 10 g per mole of silver halide, preferably, from 0.1 to 5 g per mole of silver halide.

In a preferred embodiment of the present invention, a stabilizer is added at any time before the addition of the sulfur sensitizer, preferably together with or after the metal additions. It is particularly preferred that a stabilizer is added between the metal additions and the sulfur sensitizer. In the photographic art, it is known to add a chemical stabilizer after the completion of the chemical sensitization to prevent fog or to stabilize photographic properties of the resulting photographic element during manufacture, storage or photographic processes. Even if the action of the stabilizer in the process of the present invention is not yet fully understood, it is believed that it acts as a digest stabilizer and a site director for the sulfur sensitizer. In the process of the present invention, the stabilizer is added before the addition of sulfur chemical sensitizer in an amount of from 1 to 500 milligrams per mole of silver, preferably, from 10 to 300 milligrams per mole of silver.

Specific examples of useful stabilizers include thiazole derivatives; benzothiazole derivatives; mercapto-substituted heterocyclic compounds, such as, for example, mercaptotetrazoles, mercaptotriazoles, mercaptodiazoles, mercaptopyrimidines, mercaptoazoles; azaindenes, such as triazaindenes and tetrazaaindenes; triazoles; tetrazoles; and sulfonic and sulfinic benzene derivatives. Azaindenes are preferably used in the process of the present invention, more preferably, tetraazaindenes.

Moreover, the silver halide grain emulsion may be optically sensitized to a desired region of the visible spectrum. The method for spectral sensitization is not particularly limited. For example, optical sensitization may be possible by using an optical sensitizer, including a cyanine dye, a merocyanine dye, complex cyanine and merocyanine dyes, oxonol dyes, hemioxonol dyes, styryl dyes and streptocyanine dyes, either alone or in combination. Useful optical sensitizers include cyanines derived from quinoline, pyridine, isoquinoline, benzindole, oxazole, thiazole, selenazole, imidazole. Particularly useful optical sensitizers are the dyes of the benzoxazole-, benzimidazole- and benzothiazole-carbocyanine type. Usually, the addition of the spectral sensitizer is performed after the completion of chemical sensitization. Alternatively, spectral sensitization can be performed concurrently with chemical sensitization, can entirely precede chemical sensitization, and can even commence prior to the completion of silver halide precipitation. When the spectral sensitization is performed before the chemical sensitization, it is believed that the preferential absorption of spectral sensitizing dyes on the crystallographic faces of the tabular grains allows chemical sensitization to occur selectively at unlike crystallographic surfaces of the tabular grains. In a preferred embodiment, the spectral sensitizers produce J aggregates, if adsorbed on the surface of the silver halide grains, and a sharp absorption band (J-band) with a bathochromic shift with respect to the absorption maximum of the free dye in aqueous solution.

It is known in the art of radiographic photographic elements that the intensity of the sharp absorption band (J-band) shown by the spectral sensitizing dye absorbed on the surface of the light-sensitive silver halide grains will vary with the quantity of the specific dye chosen as well as the size and chemical composition of the grains. The maximum intensity of J-band has been obtained with silver halide grains having the above described sizes and the chemical compositions absorbed with J-band spectral sensitizing dyes in a concentration of from 25 to 100 percent or more of monolayer coverage of the total available surface area of the silver halide grains. Optimum dye concentration levels can be chosen in the range of 0.5 to 20 millimoles per mole of silver halide, preferably, in the range of 2 to 10 millimoles.

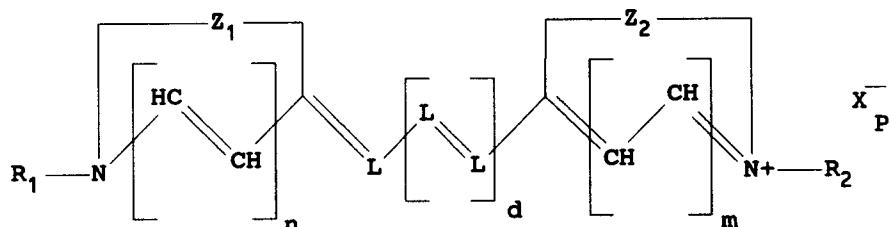
Spectral sensitizing dyes producing J aggregates are well known in the art, as illustrated by F. M. Hamer, *Cyanine Dyes and Related Compounds*, John Wiley and Sons, 1964, Chapter XVII and by T. H. James, *The Theory of the Photographic Process*, 4th Edition, MacMillan, 1977, Chapter 8.

In a preferred form, J-band exhibiting dyes are cyanine dyes. Such dyes comprise two basic heterocyclic nuclei joined by a linkage of methine groups. The heterocyclic nuclei preferably include fused benzene rings to enhance J aggregation. The heterocyclic nuclei are preferably quinolinium, benzoxazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthoxazolium, naphthothiazolium and naphthoselenazolium quaternary salts.

The cyanine dyes, which are joined by a methine linkage, include two basic heterocyclic nuclei, such as pyrrolidine, oxazoline, thiazoline, pyrrole, oxazole, thiazole, selenazole, tetrazole and pyridine and nuclei obtained by fusing an alicyclic hydrocarbon ring or an aromatic hydrocarbon ring to each of the above nuclei, such as indolenine, benzindole-5-nine, indole, benzoxazole, naphthoxazole, benzothiazole, naphthothiazole, benzoselenazole, benzimidazole and quinoline. These nuclei can have substituents groups.

The merocyanine dyes, which are joined by a methine linkage, include a basic heterocyclic nucleus of the type described above and an acid nucleus, such as a 5- or 6-membered heterocyclic nucleus derived from barbituric acid, 2-thiobarbituric acid, rhodanine, hydantoin, 2-thiohydantoin, 4-thiohydantoin, 2-pyrazolin-5-one, 2-isoxazolin-5-one, indan-1,3-dione, cyclohexane-1,3-dione, and isoquinolin-4-one.

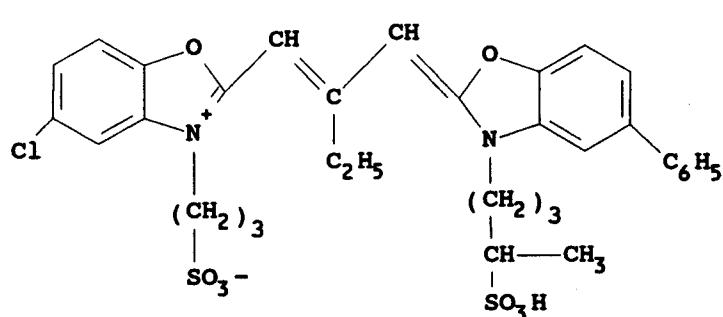
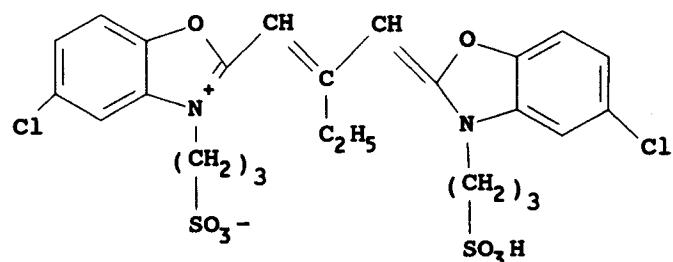
10 The preferred dyes are cyanine dyes, such as those represented by the following formula:



wherein n, m and d each independently represents 0 or 1, L represents a methine linkage, e.g., =CH-, =C(C₂H₅), etc., R₁ and R₂ each represents a substituted or unsubstituted alkyl group, preferably, a lower alkyl group of from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, butyl, cyclohexyl and dodecyl, a hydroxyalkyl group, e.g., β-hydroxyethyl and Ω-hydroxybutyl, an alkoxyalkyl group, e.g., β-methoxyethyl and Ω-butoxyethyl, a carboxyalkyl group, e.g., β-carboxyethyl and Ω-carboxybutyl, a sulfoalkyl group, e.g., β-sulfoethyl and Ω-sulfobutyl, a sulfatoalkyl group, e.g., β-sulfatoethyl and Ω-sulfatobutyl, an acyloxyalkyl group, e.g., β-acetoxyethyl, γ-acetoxypropyl and Ω-butyryloxybutyl, an alkoxy carbonyl group, e.g., β-methoxycarbonylethyl and Ω-ethoxycarbonylbutyl, benzyl, phenethyl, or an aryl group of up to 30 carbon atoms, e.g., phenyl, tolyl, xylyl, chlorophenyl and naphthyl, X represents an acid anion, e.g., chloride, bromide, iodide, thiocyanate, sulfate, perchlorate, p-toluenesulfonate and methylsulfate; the methine linkage forming an intramolecular salt when p is 0; Z₁ and Z₂, the same or different, each represents the non-metallic atoms necessary to complete the same simple or condensed 5- or 6-membered heterocyclic nucleus, such as a benzothiazole nucleus (e.g., benzothiazole, 3-, 5-, 6- or 7-chloro-benzothiazole, 4-, 5- or 6-methylbenzothiazole, 5- or 6-bromobenzothiazole, 4- or 5-phenyl-benzothiazole, 4-, 5- or 6-methoxybenzothiazole, 5,6-dimethyl-benzothiazole and 5- or 6-hydroxy-benzothiazole), a naphthothiazole nucleus (e.g., α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5-ethoxy-α-naphthothiazole and 8-methoxy-α-naphthothiazole), a benzoselenazole nucleus (e.g., benzoselenazole, 5-chloro-benzoselenazole and tetrahydrobenzoselenazole), a naphthoselenazole nucleus (e.g., α-naphtho-selenazole and β-naphthoselenazole), a benzoxazole nucleus (e.g., benzoxazole, 5- or 6-hydroxy-benzoxazole, 5-chloro-benzoxazole, 5- or 6-methoxy-benzoxazole, 5-phenyl-benzoxazole and 5,6-dimethyl-benzoxazole), a naphthoxazole nucleus (e.g., α-naphthoxazole and β-naphthoxazole), a 2-quinoline nucleus (e.g., 2-quinoline, 6-, 7, or 8-methyl-2-quinoline, 4-, 6- or 8-chloro-2-quinoline, 5-, 6- or 7-ethoxy-2-quinoline and 6- or 7-hydroxy-2-quinoline), a 4-quinoline nucleus (e.g., 4-quinoline, 7- or 8-methyl-4-quinoline and 6-methoxy-4-quinoline), a benzimidazole nucleus (e.g., benzimidazole, 5-chloro-benzimidazole and 5,6-dichloro-benzimidazole), a thiazole nucleus (e.g., 4- or 5-methyl-thiazole, 5-phenyl-thiazole and 4,5-di-methyl-thiazole), an oxazole nucleus (e.g., 4- or 5-methyl-oxazole, 4-phenyl-oxazole, 4-ethyl-oxazole and 4,5-dimethyl-oxazole), and a selenazole nucleus (e.g., 4-methyl-selenazole and 4-phenyl-selenazole. More preferred dyes within the above class are those having an internal salt group and/or derived from benzoxazole and benzimidazole nuclei as indicated before. Typical methine spectral sensitizing dyes for use in the present invention include those listed below.

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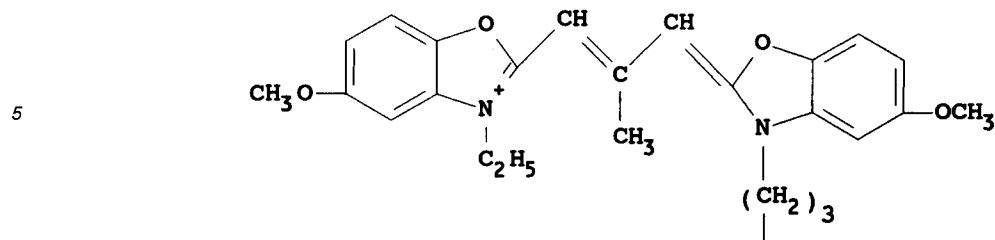
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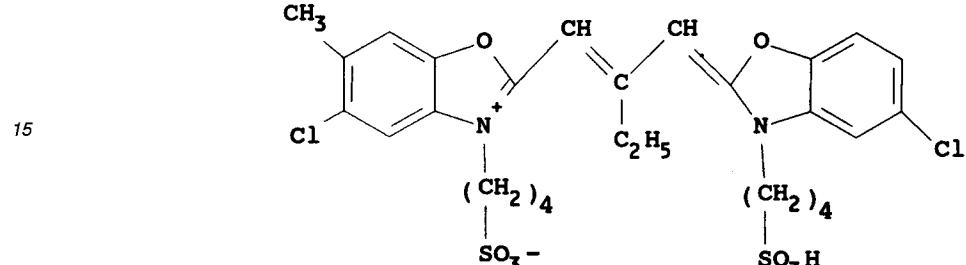
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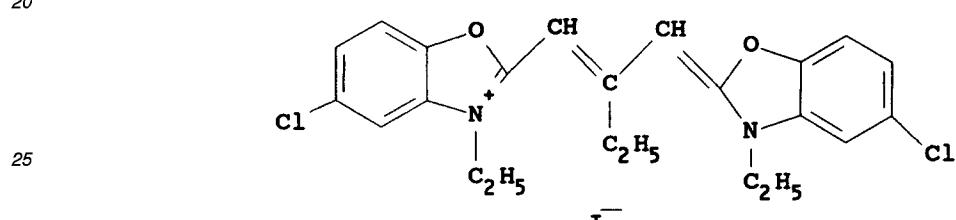
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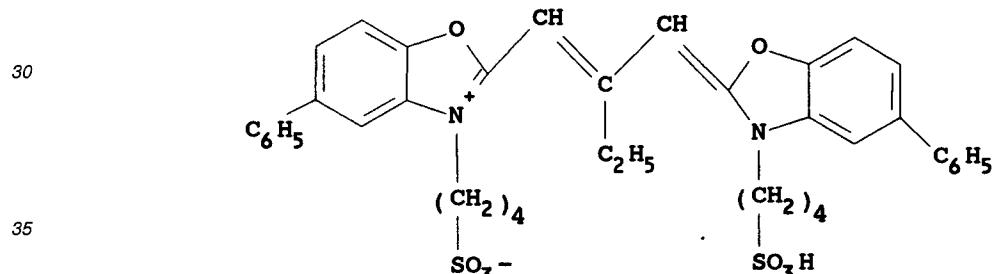
Dye C



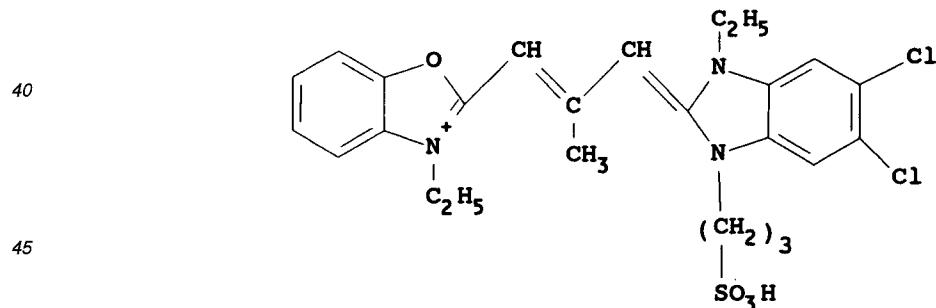
Dye D



Dye E



Dye F



Dye G

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The methine spectral sensitizing dyes are generally known in the art. Particular reference can be made to U.S. Pat. Nos. 2,503,776; 2,912,329; 3,148,187; 3,397,060; 3,573,916; and 3,822,136 and FR Pat. No. 1,118,778. Also their use in photographic emulsions is very well known wherein they are used in optimum concentrations corresponding to desired values of sensitivity to fog ratios. Optimum or near optimum concentrations of spectral sensitizing dyes generally go from 10 to 500 mg per mol of silver, preferably, from 50 to 200, and more preferably, from 50 to 100.

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Spectral sensitizing dyes can be used in combinations which result in supersensitization, i.e., spectral sensitization which is greater in a spectral region than that from any concentration of one dye alone or which would result from an additive effect of the dyes. Supersensitization can be obtained with selected combinations of spectral sensitizing dyes

and other addenda, such as stabilizers and antifoggants, development accelerators and inhibitors, optical brighteners, surfactants and antistatic agents, as described by Gilman, Photographic Science and Engineering, 18, pp. 418-430, 1974 and in U.S. Pat. Nos. 2,933,390; 3,635,721; 3,743,510; 3,615,613; 3,615,641; 3,617,295; and 3,635,721.

Various additives may be added to the emulsion depending upon their purpose. For example, stabilizers or antifoggants such as azaindenes, triazoles, tetrazoles, imidazolium salts, polyhydroxy compounds and others; developing promoters such as benzyl alcohol, polyoxyethylene type compounds, etc.; image stabilizers such as compounds of the chromane, cumaran, bisphenol type, etc.; and lubricants such as wax, higher fatty acids glycerides, higher alcohol esters of higher fatty acids, etc. may be added. Also, coating aids, modifiers of the permeability in the processing liquids, defoaming agents, antistatic agents and matting agents may be used. Other useful additives are disclosed in Research Disclosure, Item 17643, December 1978 in Research Disclosure, Item 18431, August 1979, in Research Disclosure, Item 308119, Section IV, December 1989, and in Research Disclosure Item 36544, September 1994.

As a binder for silver halide emulsions and other hydrophilic colloid layers, gelatin is preferred, but other hydrophilic colloids can be used, alone or in combination, such as, dextran, cellulose derivatives (e.g., hydroxyethylcellulose, carboxymethyl cellulose), collagen derivatives, colloidal albumin or casein, polysaccharides, synthetic hydrophilic polymers (e.g., polyvinylpyrrolidone, polyacrylamide, polyvinylalcohol, polyvinylpyrazole) and the like. Gelatin derivatives, such as, highly deionized gelatin, acetylated gelatin and phthalated gelatin can also be used. It is also common to employ the hydrophilic colloids in combination with synthetic polymeric binders and peptizers such as acrylamide and methacrylamide polymers, polymers of alkyl and sulfoalkyl acrylates and methacrylates, polyvinyl alcohol and its derivatives, polyvinyl lactams, polyamides, polyamines, polyvinyl acetates, and the like. Highly deionized gelatin is characterized by a higher deionization with respect to the commonly used photographic gelatins. Preferably, highly deionized gelatin is almost completely deionized which is defined as meaning that it presents less than 50 ppm (parts per million) of Ca^{++} and is practically free (less than 5 parts per million) of other ions such as chlorides, phosphates, sulfates and nitrates, compared with commonly used photographic gelatins having up to 5,000 ppm of Ca^{++} and the significant presence of other ions.

Other layers and additives, such as subbing layers, surfactants, filter dyes, intermediate layers, protective layers, anti-halation layers, barrier layers, dye underlayers, development inhibiting compounds, speed-increasing agents, stabilizers, plasticizers, chemical sensitizers, UV absorbers and the like can be present in the radiographic element. Dye underlayers are particularly useful to reduce the cross-over of the double coated silver halide radiographic element. Reference to well-known dye underlayer can be found in U.S. Pat. Nos. 4,900,652; 4,855,221; 4,857,446; and 4,803,150. In a preferred embodiment, a dye underlayer is coated on at least one side of the support, more preferably, on both sides of the support, before the coating of at least two silver halide emulsion.

A detailed description of photographic elements and of various layers and additives can be found in Research Disclosure 17643 December 1978, Research Disclosure 18431 August 1979, Research Disclosure 18716 November 1979, Research Disclosure 22534 January 1983, Research Disclosure 308119 December 1989, and Research Disclosure 36544, September, 1994.

Examples of materials suitable for the preparation of the support include glass, paper, polyethylene-coated paper, metals, polymeric film such as cellulose nitrate, cellulose acetate, polystyrene, polyethylene terephthalate, polyethylene, polypropylene and the like.

Another aspect of the present invention relates to a silver halide radiographic element comprising a support and at least one silver halide emulsion layer coated on both sides thereof, wherein the speed/Dmin ratio of the radiographic element is at least 26.00, preferably, at least 27.00, and more preferably, at least 28.00 when the radiographic element is exposed to X-rays under DIN 6867 Teil 1, 1995 exposure conditions through a pair of intensifying screens absorbing more than 25% of the total X-radiation and processed at 35°C in a developing and fixing solution having the composition of the following tables for 25 and 27 seconds, respectively.

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Developer			Fixer		
5 Water	g	800	(NH ₄) ₂ S ₂ O ₃	g	145.2
Na ₂ S ₂ O ₅	g	45	Na ₂ SO ₃	g	8.12
KOH 35% (w/w)	g	105	Boric Acid	g	7.00
K ₂ CO ₃	g	13.25	CH ₃ COOH	g	7.52
10 CH ₃ COOH	g	7.6	KI	g	0.05
Ethyleneglycol	g	10	CH ₃ COONH ₄	g	19.24
Diethyleneglycol	g	4.9	Al ₂ (SO ₄) ₃	g	7.74
15 Glutaraldehyde 50% (w/w)	g	7.2	H ₂ SO ₄ 100% (w/w)	g	3.58
EDTA.4Na	g	1.5	Water to make	l	1
20 BUDEX 5103.2Na 40% (w/w)	g	7.5	pH at 20°C		4.30
Boric acid	g	1.7			
25 5-methyl-benzotriazole	g	0.08			
5-nitro-indazole	g	0.107			
1-phenyl-1-H-tetrazole-5-thiol	g	0.007			
30 Hydroquinone	g	20			
Phenidone	g	1.45			
Sodium bromide	g	5			
Water to make	l	1			
35 pH at 20°C		10.35			

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Preferred light-sensitive silver halide photographic elements according to this invention are radiographic light-sensitive elements employed in X-ray imaging comprising a silver halide emulsion layer(s) coated on both surfaces of a support, preferably, a polyethylene terephthalate support. Preferably, the silver halide emulsions are coated on the support at a silver coverage in the range of 1.5 to 3 g/m² per side. Usually, the radiographic light-sensitive elements are associated with intensifying screens so as to be exposed to radiation emitted by the screens. The screens are made of relatively thick phosphor layers which transform the X-rays into more imaging-effective radiation such as light (e.g., visible light). The screens absorb a larger portion of X-rays than the light-sensitive elements do and are used to reduce the X-ray dose necessary to obtain a useful image. Intensifying screens absorbing more than 25% of the total X-radiation are preferably used with the radiographic element of the present invention. Depending from their chemical composition, the phosphors can emit radiation in the ultraviolet, blue, green or red region of the visible spectrum and the silver halide emulsions are sensitized to the wavelength region of the radiation emitted by the screens. Sensitization is performed by using spectral sensitizing dyes absorbed on the surface of the silver halide grains as described above.

More preferred light-sensitive silver halide photographic elements according to this invention are radiographic light-sensitive elements which employ intermediate diameter:thickness ratio tabular grain silver halide emulsions, as described above.

The silver halide photographic elements of the present invention are preferably fore-hardened. Typical examples of organic or inorganic hardeners include chrome salts (e.g., chrome alum, chromium acetate), aldehydes (e.g., formaldehyde and glutaraldehyde), isocyanate compounds (hexamethylene diisocyanate), active halogen compounds (e.g., 2,4-dichloro-6-hydroxy-s-triazine), epoxy compounds (e.g., tetramethylene glycol diglycidylether), N-methylol derivatives (e.g., dimethylolurea, methyloldimethyl hydantoin), aziridines, mucohalogeno acids (e.g., mucochloric acid), active vinyl derivatives (e.g., vinylsulfonyl and hydroxy-substituted vinylsulfonyl derivatives) and the like. Other references to well

known hardeners can be found in Research Disclosure, December 1989, Vol. 308, Item 308119, Section X, and Research Disclosure, September 1994, Vol. 365, Item 36544, Section II(b).

Other layers and additives, such as subbing layers, surfactants, filter dyes, intermediate layers, protective layers, anti-halation layers, barrier layers, development inhibiting compounds, speed-increasing agents, stabilizers, plasticizers, chemical sensitizers, UV absorbers and the like can be present in the radiographic element.

A detailed description of photographic elements and of various layers and additives can be found in Research Disclosure 17643 December 1978, Research Disclosure 18431 August 1979, Research Disclosure 18716 November 1979, Research Disclosure 22534 January 1983, Research Disclosure 308119 December 1989, and Research Disclosure 36544 September 1994.

The silver halide photographic element can be exposed and processed by any conventional processing technique. Any known developing agent can be added into the developer, such as, for example, dihydroxybenzenes (e.g., hydroquinone), pyrazolidones (1-phenyl-3-pyrazolidone or 4,4-dimethyl-1-phenyl-3-pyrazolidone), and aminophenols (e.g., N-methyl-p-aminophenol), alone or in combinations thereof. Preferably, the silver halide photographic elements are developed in a developer comprising dihydroxybenzenes as the main developing agent, and pyrazolidones and p-aminophenols as auxiliary developing agents.

Other well known additives can be present in the developer, such as, for example, antifoggants (e.g., benzotriazoles, indazoles, tetrazoles), silver halide solvents (e.g., thiosulfates, thiocyanates), sequestering agents (e.g., aminopolycarboxylic acids, aminopolyphosphonic acids), sulfite antioxidants, buffers, restrainers, hardeners, contrast promoting agents, surfactants, and the like. Inorganic alkaline agents, such as KOH, NaOH, and LiOH are added to the developer composition to obtain the desired pH which is usually higher than 10.

The silver halide photographic element of the present invention can be processed with a fixer of a typical composition for the application required. The fixing agents include thiosulfates, thiocyanates, sulfites, ammonium salts, and the like. The fixer composition can comprise other well known additives, such as, for example, acid compounds (e.g., metabisulfates), buffers (e.g., carbonic acid, acetic acid), hardeners (e.g., aluminum salts), tone improving agents, and the like.

The exposed radiographic elements can be processed by any of the conventional processing techniques. Such processing techniques are illustrated for example in Research Disclosure, Item 17643, cited above, and Research Disclosure 36544 September 1994. Roller transport processing is particularly preferred, as illustrated in U.S. Pat. Nos. 3,025,779; 3,515,556; 3,545,971; and 3,647,459 and in UK Patent 1,269,268. Hardening development can be undertaken, as illustrated in U.S. Patent 3,232,761.

As regards the processes for the silver halide emulsion preparation and the use of particular ingredients in the emulsion and in the light-sensitive element, reference is made to Research Disclosure, September 1994, Item 36544, and particularly to the following chapters:

- I. Emulsion grains and their preparation.
- II. Vehicles, vehicle extenders, vehicle-like addenda and vehicle related addenda.
- III. Emulsion washing.
- IV. Chemical sensitization
- V. Spectral sensitization and desensitization
- VI. UV dyes/optical brighteners/luminescent dyes
- VII. Antifoggants and stabilizers
- VIII. Absorbing and scattering materials.
- IX. Coating physical property modifying addenda.
- X. Dye image formers and modifiers.
- XI. Layers and layer arrangements
- XII. Features applicable only to color negative.
- XIII. Features applicable only to color positive.
- XV. Supports

The present invention will be now described in greater detail with reference to the following not limiting examples. All the amounts referred to in the following examples are relative to one mole of silver in the resulting silver halide emulsion, unless differently specified.

EXAMPLE 1

Sample 1 (Control)

A silver bromoiodide tabular emulsion comprising less than 0.9mol% of iodide was prepared by double jet method

using controlled pAg. The resulting emulsion had a mean grain size of 1.33 μm and an average grain thickness of 0.21 μm , thus obtaining an average aspect ratio of about 6.3. The emulsion had a coefficient of variation (COV) of about 37%.

5 Prior to starting the chemical digest, the emulsion silver concentration was first adjusted to 17 %, the pH is corrected to 6.5 and the pAg to 8.4

The emulsion was chemically and spectrally sensitized with a conventional sulfur-gold sensitization process while keeping the temperature at 60°C. The emulsion was added with 0.22 mg of mercuric chloride, 75.3 mg of Leucophor™ BCF (a polymer of bis(5-triazin-2-yl-amino-4-hydroxy-6-anilino)stilben-2,2'-sulfonic acid disodium salt), 662 mg of triethyl ammonium salt of 5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)-oxacarbocyanine as spectral sensitization dye, 265 mg of a supersensitizing copolymer of acrylamide and 4-dicyanbutadiene-diallyl-amine, 20 mg of benzothiazolium ethyl iodide, a blend of 12.4 mg of sodium para-toluenethiosulfonate dihydrate and 2.2 mg of sodium para-toluene sulfinate tetrahydrate, a blend of 9.2 mg of gold chloride and 84 mg of potassium thiocyanate, and a blend of 5 mg of potassium hexachloropalladate and 120 mg of potassium thiocyanate.

10 The digest was performed during about 120 to 130 minutes at 60°C and stabilized successively with 200 mg of potassium iodide and 1366 mg of 5-methyl-7-hydroxy-2-3-4-triazoindolizine (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) first to be chilled.

15 The sensitized silver halide emulsion was melted at 45°C and subjected to final coating digest. The resulting silver halide emulsion was immediately coated on the two faces of blue 7 mil polyester support at a coating weight of 2.25 g Ag/m² per face. An antistatic top-coat as described in EP 633,496 was provided on both emulsion layers, to obtain the 20 radiographic film sample 1. The fresh film sample 1 was kept 3 days at 38°C before being subjected to X-ray exposure between two Imation Trimax™ T8 type screens (front and back) having an X-ray absorbing power of 28%. The conditions of X-ray exposure followed the DIN 6867 Teil 1 1995. The film was then processed with Imation standard chemistry (XAD-3 developer and XAF-3 fixer) in a Imation XP-515 automatic developer at 34°C. Development and fixing times were 25 and 27 seconds, respectively. Composition of XAD-3 developer and XAF-3 fixer can be found in Table A and B.

25 The sensitometric results are reported in the following Table 1.

Sample 2 (Comparison)

30 The same emulsion of Sample 1 was chemically and spectrally sensitized with a conventional sulfur-gold sensitization process while keeping the temperature at 45°C. The following amounts are referred to one mole of silver. A blend of 2.30 mg of gold chloride and 180 mg of potassium thiocyanate were added to the emulsion. 125 mg of 5-methyl-7-hydroxy-2-3-4-triazoindolizine (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) were added after a ripening time of ten minutes; 598 mg of triethyl ammonium salt of 5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)oxacarbocyanine were added as green spectral sensitization dye after further ten minutes; finally 2.74 mg of thiosulfate pentahydrate was added in 35 the vessel as sulfuring agent.

35 The digest was performed at 45°C and stabilized successively with 200 mg of potassium iodide and 1361 mg of 5-methyl-7-hydroxy-2-3-4-triazoindolizine (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) first to be chilled.

40 The sensitized silver halide emulsion was melted at 45°C and subjected to final coating digest. A radiographic film 2 was prepared, exposed and developed according to the same procedure of Sample 1.

The sensitometric results are reported in Table 1.

Sample 3 (Invention)

45 The procedure of Sample 2 is repeated, except that the first complex solution comprised, in addition to gold chloride and potassium thiocyanate, 0.11 mg of mercuric chloride.

A radiographic film 3 was prepared, exposed and developed according to the same procedure of Sample 1.

The sensitometric results are reported in Table 1.

Sample 4 (Invention)

50 The procedure of Sample 2 is repeated, except for the three following changes (1) the first complex solution comprised, in addition to gold chloride and potassium thiocyanate, 0.11 mg of mercuric chloride; (2) the amount of the first addition of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was increased to 179 mg; and (3) the amount of the addition of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene during stabilization was reduced to 1307 mg.

55 A radiographic film 4 was prepared, exposed and developed according to the same procedure of Sample 1.

The sensitometric results are reported in Table 1.

Sample 5 (Invention)

The procedure of Sample 2 is repeated, except that the first complex solution comprised, in addition to gold chloride and potassium thiocyanate, 5.43 mg of magnesium sulfate heptahydrate.

5 A radiographic film 5 was prepared, exposed and developed according to the same procedure of Sample 1.

The sensitometric results are reported in Table 1.

Sample 6 (Invention)

10 The procedure of Sample 2 is repeated, except that the first complex solution comprised, in addition to gold chloride and potassium thiocyanate, a mixture of 0.11 mg of mercuric chloride and 5.43 mg of magnesium sulfate.

A radiographic film 6 was prepared, exposed and developed according to the same procedure of Sample 1.

The sensitometric results are reported in Table 1.

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TABLE 1

Film Sample	Dmin	Dmax	Speed	Speed/Dmin Ratio
1 (Control)	0.21	3.67	5.32	25.33
2 (Comparison)	0.24	3.58	5.56	23.16
3 (Inv.)	0.21	3.57	5.57	26.52
4 (Inv.)	0.20	3.55	5.50	27.50
5 (Inv.)	0.21	3.65	5.55	26.43
6 (Inv.)	0.20	3.70	5.58	27.90

30 It is clear from the data of Table 1 that the use of the specific components and addition order of the present invention allows to obtain a higher speed without adversely affecting Dmin, thus obtaining a more favorable speed to Dmin ratio.

Example 2

35 Sample 7 (Control)

A silver bromoiodide tabular emulsion comprising 0.9mol% of iodide was prepared by double jet method using controlled pAg. The resulting emulsion had a mean grain size of 1.38 μm and an average grain thickness of 0.21 μm , thus obtaining an average aspect ratio of about 6.6. The emulsion had a coefficient of variation (COV) of about 37%.

40 Prior to starting the chemical digest, the emulsion silver concentration is first adjusted to 17 %, the pH is corrected to 6.5 and the pAg to 8.4

The emulsion was chemically and spectrally sensitized with a conventional sulfur-gold sensitization process while keeping the temperature at 60°C. The emulsion was added with 0.22 mg of mercuric chloride, 75.3 mg of Leucophor BCF (a polymer of bis(5-triazin-2-yl-amino-4-hydroxy-6-anilino)stilben-2,2'-sulfonic acid disodium salt), 726 mg of triethyl ammonium salt of 5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)-oxacarbocyanine as spectral sensitization dye, 265 mg of supersensitizing copolymer of acrylamide and 4-dicyanbutadiene-diallyl-amine, 20 mg of benzothiazolium ethyl iodide, a blend of 12.4 mg of sodium paratoluene sulfonate dihydrate and 2.2 mg of sodium para-toluene sulfinate tetrahydrate, a blend of 9.2 mg of gold chloride and 84 mg of potassium thiocyanate, and a blend of 5 mg of potassium hexachloropalladate and 120 mg of potassium thiocyanate.

50 The digest was performed about 120 to 130 minutes at 60°C and stabilized successively with 220 mg of potassium iodide and 1366 mg of 5-methyl-7-hydroxy-2-3-4-triazoindolizine (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) first to be chilled. The sensitized silver halide emulsion is melted at 45°C and subjected to final coating digest first to be coated.

A radiographic film sample 7 was prepared, exposed and developed according to the same procedure of Sample 1. The sensitometric results are reported in Table 2.

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Sample 8 (Invention)

The same emulsion of Sample 1 was chemically and spectrally sensitized while keeping the temperature at 50°C.

Prior to start the chemical digest, the emulsion silver concentration is first adjusted to 17 %, the pH is corrected to 6.5 and the pAg to 8.25.

While keeping the temperature at 50° C, a blend of 2.49 mg gold chloride, 0.11 mg of mercuric chloride, 26 mg of zinc sulfate heptahydrate, 5 mg of potassium hexachloropalladate, and 189 mg of potassium thiocyanate were added to the emulsion. This blend constitute a complex chemical sensitizer based on a metallic salt in the presence of a thiocyanate salt that is both a silver halide solvent and a complexing agent for the metals.

After a ripening time of ten minutes, 179 mg of 5-methyl-7-hydroxy-2-3-4-triazoindolizine (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) were added; 641 mg of triethyl ammonium salt of 5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)-oxacarbocyanine were added as green spectral sensitization dye; five minutes later, 25 mg of sodium para-toluene sulfonate tetrahydrate were added as sulfide release control agent; and after further five minutes, 6.2 mg of thiosulfate pentahydrate were added in the vessel as sulfuring agent to realize complementary chemical sensitization.

The total digest time was from about 60 to 90 minutes at 50° C and stabilized successively with 200 mg of potassium iodide and 1307 mg of 5-methyl-7-hydroxy-2-3-4-triazoindolizine (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) first to be chilled.

The sensitized silver halide emulsion is melted at 45°C and subjected to final coating digest first to be coated.

A radiographic film sample 8 was prepared, exposed and developed according to the same procedure of Sample 1. The sensitometric results are reported in Table 2.

Sample 9 (Invention)

The procedure of Sample 8 is repeated, except for the following three changes: (1) the first complex solution comprised a mixture of 2.38 mg of gold chloride, 0.11 mg of mercuric chloride, 26 mg of zinc sulfate heptahydrate, and 189 mg of potassium thiocyanate; (2) 747 mg of triethyl ammonium salt of 5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)-oxacarbocyanine was used as green spectral sensitization dye; and (3) sodium para-toluene sulfinate tetrahydrate was replaced by 9 mg of benzothiazolium ethyl iodide.

The digest time was between about 60 to 90 minutes at 50° C and stabilized successively with 220 mg of potassium iodide and 1307 mg of 5-methyl-7-hydroxy-2-3-4-triazoindolizine (4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene) first to be chilled.

The sensitized silver halide emulsion is melted at 45°C and subjected to final coating digest first to be coated.

A radiographic film sample 9 was prepared, exposed and developed according to the same procedure of Sample 1. The sensitometric results are reported in Table 2.

TABLE 2

Film Sample	Dmin	Dmax	Speed	Average γ	Speed/Dmin Ratio
7 (Control)	0.215	3.49	5.43	2.73	25.26
8 (Invention)	0.205	3.66	5.56	2.59	27.12
9 (Invention)	0.200	3.55	5.69	2.65	28.45

TABLE A

Developer		
Water	g	800
Na ₂ S ₂ O ₅	g	45
KOH 35% (w/w)	g	105
K ₂ CO ₃	g	13.25
CH ₃ COOH	g	7.6
Ethyleneglycol	g	10
Diethyleneglycol	g	4.9
Glutaraldehyde 50% (w/w)	g	7.2
EDTA.4Na	g	1.5
BUDEX 5103.2Na 40% (w/w)	g	7.5
Boric acid	g	1.7
5-methyl-benzotriazole	g	0.08
5-nitro-indazole	g	0.107
1-phenyl-1-H-tetrazole-5-thiol	g	0.007
Hydroquinone	g	20
Phenidone	g	1.45
Sodium bromide	g	5
Water to make	l	1
pH at 20°C		10.35

TABLE B

Fixer		
(NH ₄) ₂ S ₂ O ₃	g	145.2
Na ₂ SO ₃	g	8.12
Boric Acid	g	7.00
CH ₃ COOH	g	7.52
KI	g	0.05
CH ₃ COONH ₄	g	19.24
Al ₂ (SO ₄) ₃	g	7.74
H ₂ SO ₄ 100% (w/w)	g	3.58
Water to make	l	1
pH at 20°C		4.30

Claims

1. A process for chemically sensitizing a silver halide photographic emulsion comprising the following steps:
 - (a) adding to a silver halide photographic emulsion a noble metal and at least one metal selected from the group consisting of Group II metals, Group VIII metals, and Group IIB metals, and thereafter
 - (b) adding to said silver halide photographic emulsion a sulfur sensitizer.
2. The process according to claim 1, wherein said noble metal is gold.
3. The process according to claim 1, wherein said Group II metals are selected from the group consisting of Mg and Ca.
4. The process according to claim 1, wherein said Group VII metals are selected from the group consisting of Pd, Co, and Ni.
5. The process according to claim 1, wherein said Group IIB metals are selected from the group consisting of Zn and Hg.

6. The process according to claim 1, wherein said sulfur sensitizer is selected from the group consisting of thiosulfate, thiourea, rhodanine, and triphenylthiophosphine.

5 7. The process according to claim 1, wherein a silver halide solvent is added at any time before the addition of said sulfur sensitizer.

10 8. The process according to claim 7, wherein said silver halide solvent is added before or together with the addition of said step (a).

15 9. The process according to claim 8, wherein said silver halide solvent is selected from the group consisting of ammonia, thioether derivatives, thiocyanate derivatives and salts thereof, and ammonium and alkali halides.

10 10. The process according to claim 8, wherein said silver halide solvent is a thiocyanate derivative or salt thereof.

15 11. The process according to claim 1, wherein at least one stabilizer is added at any time before the addition of said sulfur sensitizer.

20 12. The process according to claim 11, wherein said at least one stabilizer is added together with or after the addition of said step (a).

13. The process according to claim 12, wherein said at least one stabilizer is selected from the group consisting of thiazole derivatives; benzothiazole derivatives; mercapto-substituted heterocyclic compounds; azaindenes; triazoles; tetrazoles; and sulfonic and sulfinic benzene derivatives.

25 14. The process according to claim 1, wherein a silver halide solvent and at least one stabilizer are added at any time before the addition of said sulfur sensitizer.

15. The process according to claim 14, wherein a silver halide solvent is added before or together with the addition of said step (a) and a stabilizer is added together with or after the addition of said step (a).

30 16. The process according to claim 14, wherein the addition components are added in the following order:

35 (i) said silver halide solvent,
(ii) said noble metal and metal(s) selected from the group consisting of Group II metals, Group VIII metals, and Group IIB metals,
(iii) said stabilizer(s), and
(iv) said sulfur sensitizer.

17. The process according to claim 14, wherein the addition components are added in the following order:

40 (i) said silver halide solvent, noble metal and metal(s) selected from the group consisting of Group II metals, Group VIII metals, and Group IIB metals,
(ii) said stabilizer(s), and
(iii) said sulfur sensitizer.

45 18. A silver halide radiographic element comprising a support and at least one silver halide emulsion layer coated on both side thereof, wherein the speed/Dmin ratio of said radiographic element is at least 26.00 when said radiographic element is exposed to X-rays under DIN 6867 Teil 1, 1995 exposure conditions through a pair of intensifying screens absorbing more than 25% of the total X-radiation and processed at 35°C in developing and fixing solutions having the following composition for 25 and 27 seconds, respectively

Developer		
Water	g	800
Na ₂ S ₂ O ₅	g	45
KOH 35% (w/w)	g	105
K ₂ CO ₃	g	13.25
CH ₃ COOH	g	7.6
Ethyleneglycol	g	10
Diethyleneglycol	g	4.9
Glutaraldehyde 50% (w/w)	g	7.2
EDTA.4Na	g	1.5
BUDEX 5103.2Na 40% (w/w)	g	7.5
Boric acid	g	1.7
5-methyl-benzotriazole	g	0.08
5-nitro-indazole	g	0.107
1-phenyl-1-H-tetrazole-5-thiol	g	0.007
Hydroquinone	g	20
Phenidone	g	1.45
Sodium bromide	g	5
Water to make	l	1
pH at 20°C		10.35

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Fixer		
(NH ₄) ₂ S ₂ O ₃	g	145.2
Na ₂ SO ₃	g	8.12
Boric Acid	g	7.00
CH ₃ COOH	g	7.52
KI	g	0.05
CH ₃ COONH ₄	g	19.24
Al ₂ (SO ₄) ₃	g	7.74
H ₂ SO ₄ 100% (w/w)	g	3.58
Water to make	l	1
pH at 20°C		4.30



European Patent
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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y	EP 0 368 304 A (FUJI) * page 7, line 56 - page 8, line 40 * * page 13, line 35 - page 14, line 5 * ---	1-17	G03C1/08 G03C1/09 G03C5/17
Y	US 5 294 532 A (ITO ET AL.) * column 6, line 13 - line 52 * * column 29, line 29 - line 32 * ---	1-17	
Y	EP 0 438 135 A (FUJI) * page 3, line 52 - line 55 * * page 4, line 3 - line 8 * * page 4, line 55 - line 57 * * page 5, line 14 - line 32 * * page 32, line 8 - line 13 * * page 33, line 28 - line 34 * ---	1-3,6-16	
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A	EP 0 661 592 A (3M) * page 12, line 26 - page 13, line 48 * ---	18	
A	EP 0 559 061 A (3M) * page 9, line 23 - page 11, line 15 * -----	18	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	14 November 1997	Magrizos, S	
CATEGORY OF CITED DOCUMENTS		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	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**CLAIMS INCURRING FEES**

The present European patent application comprised at the time of filing more than ten claims.

Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):

No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

SEE SHEET B

All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions, or groups of inventions, namely:

1. Claims 1-17 : Sensitisation process of silver halide photographic emulsion.
2. Claim 18 : Silver halide radiographic material with specific sensitometric characteristics.