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(54) Process for the preparation of silver halide photographic element

(57) The present invention relates to a process for the manufacturing of a silver halide element comprising a silver halide emulsion-making step, a chemical and optical sensitization step, and a silver halide emulsion coating step, characterized in that said process comprises the step of adding to said silver halide emulsion, before the coating step, an aryl compound having at least two hydroxyl groups and at least one additional substituent represented by a sulfonic group, an hydroxyl group, a carboxy group or an hydroxymethyl group in an amount of less than 0.03 moles per mole of silver. The use of such an aryl compound agent to prevent metal contamination of a silver halide photographic emulsion and a silver halide emulsion and element comprising such an aryl compound is also claimed.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a process for preparing a silver halide photographic element. In particular, the present invention relates to the use of an aryl derivative in a process for the preparation of a silver halide photographic element to reduce or eliminate spot defects in the photographic element due to metallic contamination.

BACKGROUND OF THE INVENTION

[0002] 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).

[0003] Afterwards, the silver halide emulsions are subjected to a sensitization process for increasing their sensitivity to light. There are two primary methods for sensitization: spectral sensitization and chemical sensitization.

[0004] Spectral sensitization comprises the addition of spectral sensitizing dyes which can be adsorbed on the silver halide grain surface to make the emulsion sensitive to the imaging or phosphor emitted radiation, typically visible or infrared radiation.

[0005] Chemical sensitization involves 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.

[0006] A number of patents and patent applications, as well as literature references disclose specific methods to improve chemical sensitization. See i.e., Research Disclosure, September 1994, Item 36544, Paragraph IV, pp. 510-511, which gives a wide array of references for each of the above-mentioned methods.

[0007] After the sensitization process, the silver halide emulsion is coated onto a support together with coating additives. A wide description of useful coating aids can be found in Research Disclosure No. 38597, September 1996, "Photographic Silver Halide Emulsions, Preparations, Addenda, Systems and Processing", Item IX.

[0008] In the preparation of silver halide elements, one needs to take care that the elements are free from any metal contamination. For example, fine metal particles may be produced by the equipment during the manufacturing process. Metal contamination can occur during any step from the base preparation to final coating. Even though different metals like copper or nickel can be present in the final material, the main metal contaminant is fine iron particles. The presence of iron ions like Fe (III) can desensitize the silver halide and produce a lower density halo on the developed film appearing as a white spot. The presence of fine metallic iron particles or iron ions like Fe (II) can generate, by oxidation, the release of one or two electrons, which produce a sensitized halo on the developed film appearing as black spots. The terms white or black spot are relative terms merely meaning that the spot either appears whiter or blacker than the surrounding non contaminated area of the film. White and/or black spots in a developed image give rise to poor image quality and are unacceptable in many photographic films, especially, in an X-ray application where spots interfere with medical diagnosis. One approach used in the art to control or eliminate these defects is to add a sequestering or chelating agent. The chemical compound generally forms a strong complex with the metal so that the metal can be removed from the photosensitive element thus preventing spot formation. Several different types of complexing agents have been described in the art.

[0009] US Patent 3,443,951 discloses the use of phosphoric acid esters in photographic element to prevent spot formation caused by metal particles.

[0010] US Patent 4,340,665 discloses the use of phosphate and amine complexing agents in synergistic combination to reduce spot formation caused by iron contamination of photographic element.

[0011] US Patent 3,925,086 discloses the use of azotriazoles and azotetrazoles as antispot agent in photographic silver halide emulsion or in processing baths.

[0012] US Patent 3,300,312 discloses the use of sulfosalicylic acid in photographic elements to reduce spotting from metallic particles.

[0013] EP 733,940 discloses the use of both phosphate and sulfosalicylic acid in photographic elements to reduce spotting from spurious metal particle contamination.

[0014] GB Patent 1,350,303 discloses the use of thienyl or furyl compound to reduced tendency to spot formation due to metal or metal oxide contamination.

[0015] GB Patent 1,350,302 discloses the use of aldoxime compound to reduced tendency to spot formation due to metal or metal oxide contamination.

[0016] US Patent 4,340,665 discloses the use of phosphate and hydroxyethylene diamine triacetate in photographic silver halide materials to reduce metal particle contamination.

[0017] Even though these methods provide substantial spot decrease, loss of sensitometric properties is usually observed. Therefore, there is a need for materials that reduce spot defects due to metallic contamination without deteriorating the sensitometric properties.

[0018] Even though hydroxy-substituted aryl compounds have been introduced into silver halide emulsions, the function of the materials in the emulsions are for a variety of purposes non-related to metal contaminants.

[0019] US 5,028,520 discloses the use of hydroquinone sulfonic acid potassium salt on tabular silver halide emulsion in an amount of from 0.03 to 0.5 moles per mole of silver to decrease the surface glossiness. It is also disclosed that no effect is obtained with amount lower than 0.03 mole per mole of silver.

[0020] JP 54-040729, JP 56-001936 and JP 62-021143 disclose the use of polyhydroxybenzene derivatives on cubic silver halide emulsions to decrease pressure sensitivity in graphic art films.

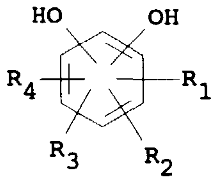
[0021] EP 452772, EP 476521, EP 482599 and EP 488029 disclose the use of polyhydroxybenzene derivatives with functional groups that allow better silver halide grain adsorption to decrease pressure sensitivity of final film.

[0022] EP 339870 discloses a silver halide photographic emulsion having in reactive association a sensitizing amount of polyalkylene glycol compound and a fog reducing amount of an arylhydroxy compound.

SUMMARY OF THE INVENTION

[0023] The present invention provides a process for manufacturing a silver halide photographic element comprising the step of adding an aryl compound having at least two hydroxyl groups and at least one additional substituent represented by a sulfonic group, an hydroxyl group, a carboxy group or a hydroxymethyl group in an amount less than 0.03 moles per mole of silver to a silver halide emulsion before coating onto a support base. The addition of the aryl compound reduces or eliminates spot defects due to metallic contamination of a silver halide photographic emulsion comprising silver halide tabular grains.

[0024] The aryl compound is represented by the following formula:



wherein R_1 to R_4 are selected from the group consisting of a hydrogen atom, a sulfonic group, an hydroxyl group, a carboxy group and an hydroxymethylene group, provided that at least one of R_1 to R_4 is different from hydrogen atom.

[0025] In another embodiment of the present invention, a silver halide photographic material is provided comprising a support based having coated thereon at least one silver halide emulsion layer, wherein said silver halide emulsion layer comprises an aryl compound having at least two hydroxyl groups and at least one additional substituent represented by a sulfonic group, an hydroxyl group, a carboxy group or an hydroxymethyl group in an amount less than 0.03 moles per mole of silver.

DETAILED DESCRIPTION OF THE INVENTION

[0026] The process for manufacturing silver halide elements typically involves an emulsion-making step, a chemical and optical sensitization step, and a coating step.

[0027] The silver halide emulsion-making step generally comprises (i) a nucleation step, where silver halide grain seeds are formed, (ii) one or more growing steps, where the grain seeds achieve their final dimension, and (iii) a washing step, where all soluble salts are removed from the final emulsion. In addition, a ripening step is usually performed between the nucleation and growing step and/or between the growing and the washing steps.

[0028] 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 example, 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 of the grains, and the grain-growth rate. General guidance for these procedures may be found in the following references 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; Chime 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); US Pat. Nos. 2,222,264; 2,592,250; 3,650,757; 3,917,485; 3,790,387; 3,716,276; and 3,979,213; and Research Disclosure, Sept. 1994, Item 36544 "Photographic Silver Halide Emulsions, Preparations, Addenda, Systems and Processing."

[0029] In the preparation of silver halide emulsions, 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 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 1.5mol% silver iodide. The halogen composition of individual grains may be homogeneous or heterogeneous.

[0030] As a binder for silver halide emulsions, 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.

[0031] The grains of these silver halide emulsions may be coarse or fine, and the grain size distribution of them may be narrow or broad. In addition, 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 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.

[0032] Preferably, tabular silver halide emulsions are used 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. As used herein, aspect ratio refers to the average diameter:thickness ratio of the silver halide grains. Average diameters of the tabular silver halide grains 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 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.

[0033] 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" refers to 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.

[0034] 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.

[0035] Examples for the preparation of silver halide emulsions containing tabular silver halide grains are described 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; 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; Berry et al., "Effects of Environment on the Growth of Silver Bromide Microcrystals", Vol.5, No.6 (1961), pp. 332-336; Research Disclosure, Sept. 1994, Item 36544 "Photographic Silver Halide Emulsions, Preparations, Addenda, Systems and Processing"; US 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 EP Pat. Appln. No. 263,508.

[0036] At the end of the silver halide grain formation, water soluble salts are removed from the emulsion by procedures generally known by those skilled 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.

[0037] 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.

[0038] Prior to use, silver halide grain emulsions are generally fully dispersed and bulked up with gelatin or other dispersion of peptizer and subjected to any of the known methods for achieving optimum sensitivity. A wide description of methods and compounds useful in chemical and optical sensitization may be found in Research Disclosure No. 38597, September 1996, "Photographic Silver Halide Emulsions, Preparations, Addenda, Systems and Processing", Items IV and 5.

[0039] Chemical sensitization is performed by adding chemical sensitizers and other additional compounds to the silver halide emulsion, followed by the so-called chemical ripening at high temperature for a predetermined period of time. Chemical sensitization can be performed by a variety of chemical sensitizers such as gold, sulfur, reducing agents, platinum, selenium, sulfur plus gold, and the like. Tabular silver halide grains, after grain formation and desalting, are preferably chemically sensitized by at least one gold sensitizer and at least one sulfur sensitizer. During chemical sensitization other compounds can be added to improve the photographic performances of the resulting silver halide emulsion, such as, for example, antifoggants, stabilizers, optical sensitizers, supersensitizers, and the like.

[0040] Gold sensitization is performed by adding a gold sensitizer to the emulsion and stirring the emulsion at high temperature of preferably 40°C or more for a predetermined period of time. As a gold sensitizer, any gold compound which has an oxidation number of +1 or +3 and is normally used as gold sensitizer can be used. Preferred examples of gold sensitizers are chloroauric acid, the salts thereof and gold complexes, such as those described in US 2,399,083. Specific examples of gold sensitizers include chloroauric acid, potassium chloroaurate, auric trichloride, sodium aurithiosulfate, potassium aurithiocyanate, potassium iodoaurate, tetracyanoauric acid, 2-aurosulfobenzothiazole methochloride and ammonium aurothiocyanate.

[0041] Sulfur sensitization is performed by adding a sulfur sensitizer to the silver halide emulsion and stirring the emulsion at a high temperature of 40°C or more for a predetermined period of time. Useful examples of sulfur sensitizer include thiosulfonates, thiocyanates, sulfinates, thioethers, and elemental sulfur.

[0042] The amounts of the gold sensitizer and the sulfur sensitizer change in accordance with the various conditions, such as activity of the gold and sulfur sensitizer, type and size of silver halide grains, temperature, pH and time of chemical ripening. These amounts, however, are preferably from 1 to 20 mg of gold sensitizer per mole of silver, and from 1 to 100 mg of sulfur sensitizer per mole of silver. The temperature of chemical ripening is preferably 45°C or more, and more preferably 50°C to 80°C. The pAg and pH may take arbitrary values.

[0043] During chemical sensitization, times and order of addition of the gold sensitizer and sulfur sensitizer are not particularly limited. For example, gold and sulfur sensitizers can be added at the initial stage of chemical sensitization or at a later stage either simultaneously or at different times. Usually, gold and sulfur sensitizers are added to the silver halide emulsion as aqueous solutions, in a water-miscible organic solvent, such as methanol, ethanol and acetone, or mixtures thereof.

[0044] A stabilizer is preferably added at any time before the addition of the sulfur sensitizer. Even if the action of the stabilizer is not yet fully understood, it is believed that it acts as a digest stabilizer and a site director for the sulfur sensitizer. Preferably, 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.

[0045] 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 tetrazaindenes; triazoles; tetrazoles; and sulfonic and sulfinic benzene derivatives. Azaindenes are preferably used, more preferably, tetraazaindenes.

[0046] 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 achieved 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 may be performed concurrently with chemical sensitization, entirely precede chemical sensitization, or 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.Preferably, 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.

[0047] 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.

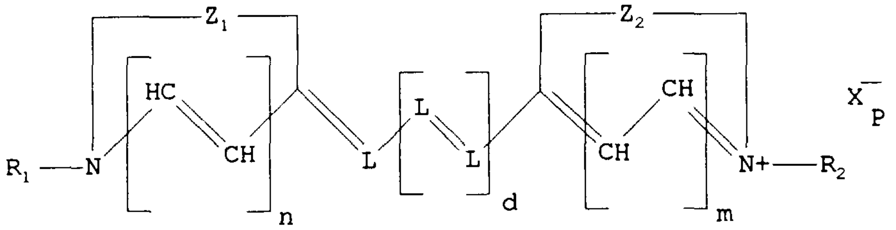
[0048] Spectral sensitizing dyes producing J aggregates are well known in the art, as illustrated by F. M. Hamer, ***Cyanine Dyes and Related Compounds***, John Wiley and Sons, 1964, Chapter XVII and by T. H. James, ***The Theory of the Photographic Process***, 4th Edition, MacMillan, 1977, Chapter 8.

[0049] In a preferred form, J-band exhibiting dyes are cyanine dyes having two basic heterocyclic nuclei joined by a linkage of methine groups. The heterocyclic nuclei preferably include fused benzene rings to enhance J aggregation. Preferred heterocyclic nuclei include quinolinium, benzoxazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthoxazolium, naphthothiazolium and naphthoselenazolium quaternary salts.

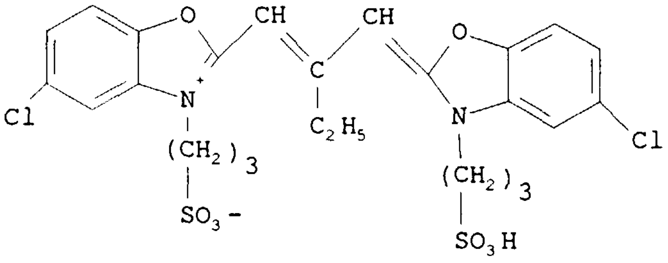
[0050] The cyanine dyes, which are joined by a methine linkage, include two basic heterocyclic nuclei, such as pyrrolidine, oxazoline, thiazoline, pyrrole, oxazole, thiazole, selenazole, tetrazole and pyridine and nuclei obtained by fusing an alicyclic hydrocarbon ring or an aromatic hydrocarbon ring to each of the above nuclei, such as indolenine, benzindolenine, indole, benzoxazole, naphthoxazole, benzothiazole, naphthothiazole, benzoselenazole, benzimidazole and quinoline. These nuclei can have substituents groups.

[0051] 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.

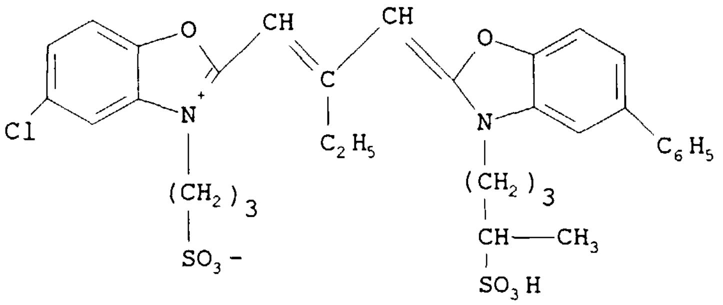
[0052] The preferred dyes are cyanine dyes, such as those represented by the following formula:



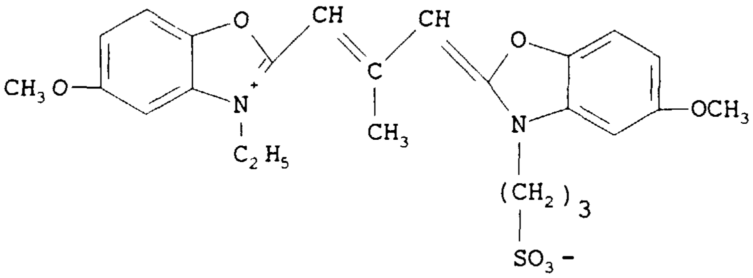
wherein n, m and d each independently represents 0 or 1, L represents a methine linkage, e.g., =CH-, ≡C(C_2H_5), etc., R_1 and R_2 each represents a substituted or unsubstituted alkyl group, preferably, a lower alkyl group of from 1 to 4 carbon atoms, e.g., methyl, ethyl, propyl, butyl, cyclohexyl and 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 alkoxycarbonylalkyl 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; Z_1 and Z_2, 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 include those listed below.



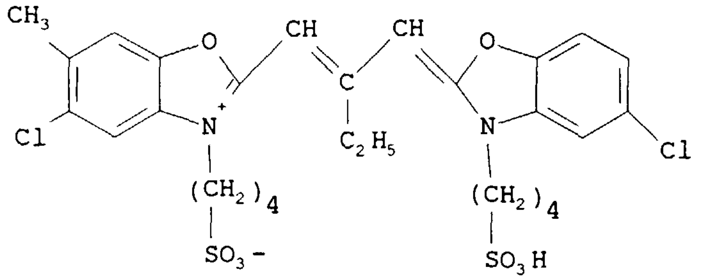
Dye A



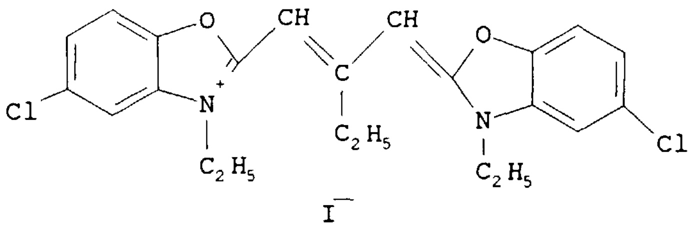
Dye B



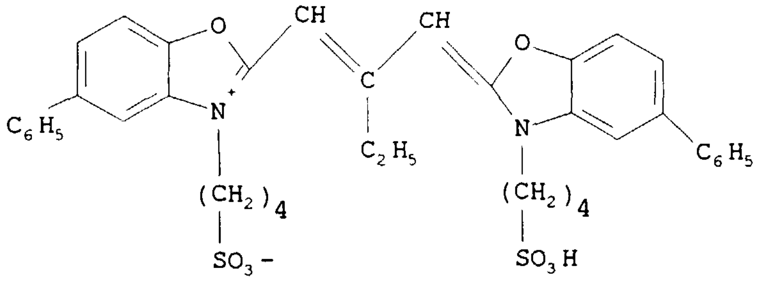
Dye C



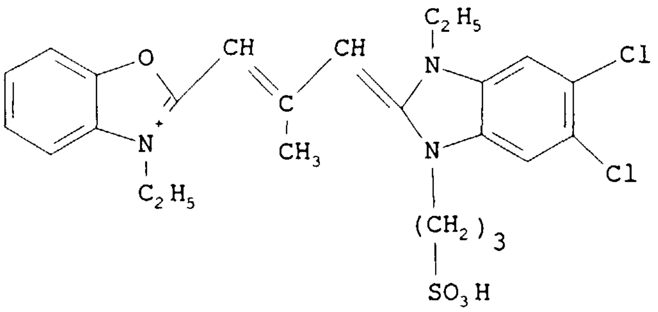
Dye D



Dye E



Dye F



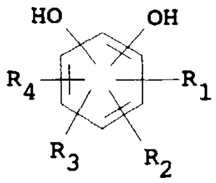
Dye G

[0053] The methine spectral sensitizing dyes are generally known in the art. Particular reference can be made to US 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 mole of silver, preferably, from 50 to 200, and more preferably, from 50 to 100.

[0054] 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 US Pat. Nos. 2,933,390; 3,635,721; 3,743,510; 3,615,613; 3,615,641; 3,617,295; and 3,635,721.

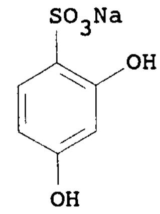
[0055] The resulting silver halide emulsion is then coated on a proper support to prepare a silver halide photographic material. According to the method of the present invention, an aryl compound having at least two hydroxyl groups and at least one additional substituent represented by a sulfonic group, an hydroxyl group, a carboxy group or an hydroxymethyl group is added to the silver halide emulsion in an amount of less than 0.03 moles per mole of silver before coating the silver halide emulsion onto the support base.

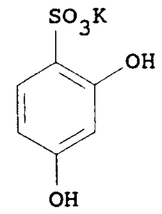
[0056] The aryl compound is represented by the following formula:

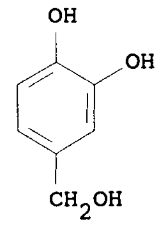


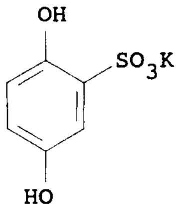
wherein R_1 to R_4 are selected from the group consisting of a hydrogen atom, a sulfonic group, an hydroxyl group, a carboxy group and an hydroxymethylene group, provided that at least one of R_1 to R_4 is different from hydrogen atom.

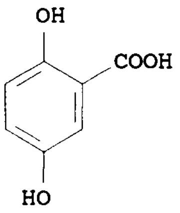
[0057] Suitable aryl compounds represented by the above-referenced general formula include the following:

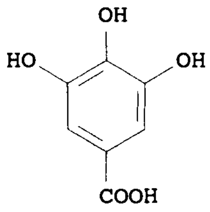

SO$_3$Na
OH
OH

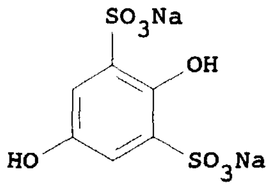

SO$_3$K
OH
OH

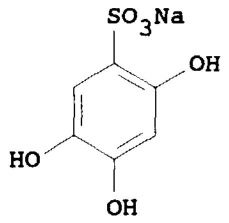

OH
OH
CH$_2$OH

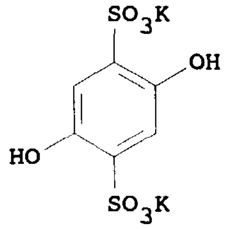

OH
SO$_3$K
HO


OH
COOH
HO


OH
HO
OH
COOH







[0058] The amount of the above described aryl compound is preferably in the range of from 0.0001 to 0.03 moles per mole of silver, more preferably from 0.001 to 0.03 moles per mole of silver, and most preferably from 0.005 to 0.03 moles per mole of silver.

[0059] The use of the above described aryl compounds alllows to reduce or eliminate spot defects due to metallic contamination of a silver halide photographic emulsion. Metallic contamination is due to the presence of metals, in particular heavy metals, such as iron, copper, chromium, tin, nickel, and also aluminium. Such metals contaminate the emulsion during the various steps of preparation, coating and/or storage and cause sensitization or desensitization of the silver halide grains, thus causing the appearance of black or white spot in the developed photographic material. The aryl compounds used in the present invention are able to chelate the metal ions so reducing the concentration of free metal ions to a harmless level. The resulting metal-contaminate free silver halide emulsion comprises less than 1 micromoles of free metal ions per gram of emulsion.

[0060] Other additives can be added to the silver halide emulsion before or during coating, such as, 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; Research Disclosure, Item 18431, August 1979; Research Disclosure, Item 308119, Section IV, December 1989; and Research Disclosure Item 36544, September 1994.

[0061] Suitable support materials include glass, paper, polyethylene-coated paper, metals, polymeric film such as cellulose nitrate, cellulose acetate, polystyrene, polyethylene terephthalate, polyethylene, polypropylene and the like.

[0062] Preferred light-sensitive silver halide photographic elements 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/m^2 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. 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.

[0063] 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 may be found in US Pat. Nos. 4,900,652; 4,855,221; 4,857,446; and 4,803,150.Preferably, 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.

[0064] The silver halide radiographic elements 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).

[0065] 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.

[0066] 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 arninophenols (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.

[0067] 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.

[0068] The silver halide photographic element 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.

[0069] 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 useful, such as those illustrated in US 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 achieved, as illustrated in US Patent 3,232,761.

[0070] With regards to 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 1996, Item 38957, 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
XV. Supports

[0071] 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)

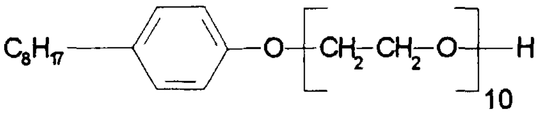
[0072] A silver bromoiodide emulsion with an average grain equivalent diameter of 1.25 micron, an average grain thickness of 0.18 micron, a COV of 37 % and 0.9 percent iodide in mole respect to the total halide ions was prepared by double jet method.

[0073] The emulsion was chemically and spectrally sensitized using sulfur, gold, mercury and palladium sensitizers plus a triethyl ammonium salt of 5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl) oxacarbocyanine as spectral sensitization dye. The digest was performed about 120 to 130 minutes at 60° 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) before chilling.

[0074] The sensitized silver halide emulsion was melted at 45°C and subjected to coating finals in laboratory. As coating auxiliaries were added 1293 mg of calcium nitrate, 80 mg of azodicarboxylic dimorpholide, 18338 mg of polyethylacrylate (in dispersion at 20% in water plus 367 mg of lauryl sulfate), 66738 mg of dextran (manufactured by Pharmacosmos) as gel extender, 267 mg of Colanyl blue™ (manufactered by Hoechst Chemical Co.) as chromatic corrector. The pH was corrected to 6.3 before adding 3774 mg of SSMA copolymer (copolymer of Styrene sulfonic acid and maleic anhydride, manufactured by Aquaness Corp., Texas, USA).

[0075] The resulting silver halide emulsion was immediately coated on the two faces of blue 7 mil polyester base code with a conventional antistatic top-coat containing hardening agents. The coating speed was 8.3 meters per minute and the covering weight was around 2.25 g of silver per m^2 per side.

[0076] The fresh film sample was kept 3 days at 38°C before being subjected to iron (III) contamination. This was done by applying on one side and at the rate of 11.4 ml per square meter a solution containing 0.1% by weight ferric sulfate $Fe_2(SO_4)_3$ as iron source, 1% standard gelatin (manufactured by Deutche Gelatin Fabrik AG, Germany) as coating auxiliary and 0.12% Triton™ X 100 as surfactant. This solution is coated on half surface of a 10 by 28 cm sheet with a Mayer bar number five. This method allows to ensure that a determined level of contaminant is present and to make discernible the compounds that are capable of removing defects caused by the contaminant. Triton™ is a non-ionic surfactant of the alkylphenoxyethylene type having the following formula:



[0077] The contaminated film was dried and exposed to white light with a standard bromograph for 3/10 of second with filter number 8.

[0078] The exposed films were processed through a 90 seconds dry to dry medical X-ray automatic processor type XP 515 (manufactured by IMATION Corp., MN, USA) with standard chemistry (XAD 3 developer and XAF 3 fixer, both manufactured by IMATION Corp., MN, USA).

[0079] The optical densities are measured on both the non-contaminated and the contaminated areas and the desensitizing effect of iron (III) is determined using the following formula:

$\Delta D \% = (D1-D2)*100/D2$, with D1 representing the average value of 10 density measurements on the contaminated area of the material and D2 representing the average value of 10 density measurements on the non-contaminated area of the same sheet.

[0080] The value of ΔD % is negative if there is a desensitization effect, positive if there is a sensitization effect of the contaminant, and is proportional to the resulting effect of iron contamination on the final material which has not antispot protection. The results are reported in the following Table 1.

Sample 2 (Invention)

[0081] The procedure of sample 1 is repeated, except that during addition of coating finals, 5 g of compound 1 (2,5-dihydroxybenzenesulfonic acid potassium salt) is added per one mole of silver, corresponding to 0.0219 moles of compound per mole of silver and 209 mg of compound per square meter of coated film. The iron contamination process is carried out in the same manner on the half sheet to determine the protection effect of compound 1. The results are reported in the following Table 1.

Sample 3 (Invention)

[0082] The procedure of sample 1 is repeated, except that during addition of coating finals, 7.55 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0218 moles of compound per mole of silver and 315 mg of compound per square meter of coated film. The iron contamination process is carried out in the same manner on the half sheet to determine the protection effect of compound 2. The results are reported in the following Table 1.

TABLE 1

Sample	Compound	Contaminant Amount (mmol/m2/side)	ΔD%
1 (C)	-	0.06	- 6.0
2 (I)	1	0.06	- 1.5
3 (I)	2	0.06	- 0.5

[0083] The control sample 1 shows the desensitizing effect of 0.06 millimole per square meter of iron (III). The invention samples 2 and 3 clearly show that the aryl compounds described in the present invention are able to reduce the negative effect of iron (III).

Example 2

Sample 4 (control)

[0084] The procedure of sample 1 is repeated, except that the fresh film sample was kept 3 days at 38°C before being subjected to copper (II) contamination using 11.4 ml per m^2 of a solution containing 0.5% by weight cupric nitrate $Cu(NO_3)_2$ as copper source, 1% standard gelatin (manufactured by Deutsche Gelatin Fabrik AG, Germany) as coating auxiliary, 0.12% of Triton™ X 100 as surfactant coated on half the surface of a 10 by 28 cm sheet with a Mayer bar number five. The results are reported in the following Table 2.

Sample 5 (Invention)

[0085] The procedure of sample 4 is repeated, except that during addition of coating finals, 5 g of compound 1 (2.5-dihydroxybenzenesulfonic acid potassium salt) is added per one mole of silver, corresponding to 0.0219 moles of compound per mole of silver and 209 mg of compound per square meter of coated film. The copper contamination process is carried out in the same manner on the half sheet to determine the protection effect of compound 1. The results are reported in the following Table 2.

Sample 6 (Invention)

[0086] The procedure of sample 4 is repeated, except that during addition of coating finals, 7.55 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0218 moles of compound per mole of silver and 315 mg of compound per square meter of coated film. The copper contamination process is carried out in the same manner on the half sheet to determine the protection effect of compound 2. The results are reported in the following Table 2.

TABLE 2

Sample	Compound	Contaminant Amount (mmol/m2/side)	ΔD%
4 (C)	-	0.48	- 37
5 (I)	1	0.48	- 26
6 (I)	2	0.48	- 19

[0087] Samples 5 and 6 clearly show that the aryl compounds described in the present invention are able to reduce the negative effect of copper (II).

Example 3

Sample 7 (Control)

[0088] The procedure of sample 1 is repeated. The results are reported in the following Table 3.

Sample 8 (Invention)

[0089] The procedure of sample 7 is repeated, except that during addition of coating finals, 2 g of compound 3 (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0064 moles of compound per mole of silver and 83 mg of compound per square meter of coated film. The results are reported in the following Table 3.

Sample 9 (Invention)

[0090] The procedure of sample 7 is repeated, except that during addition of coating finals, 4 g of compound 3 (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0128 moles of compound per mole of silver and 166 mg of compound per square meter of coated film. The results are reported in the following Table 3.

Sample 10 (Invention)

[0091] The procedure of sample 7 is repeated, except that during addition of coating finals, 8 g of compound 3 (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0256 moles of compound per mole of silver and 333 mg of compound per square meter of coated film. The results are reported in the following Table 3.

Sample 11 (Invention)

[0092] The procedure of sample 7 is repeated, except that during addition of coating finals, 2.21 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0064 moles of compound per mole of silver and 92 mg of compound per square meter of coated film. The results are reported in the following Table 3.

Sample 12 (Invention)

[0093] The procedure of sample 7 is repeated, except that during addition of coating finals, 4.42 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0128 moles of compound per mole of silver and 184 mg of compound per square meter of coated film. The results are reported in the following Table 3.

Sample 13 (Invention)

[0094] The procedure of sample 7 is repeated, except that during addition of coating finals, 8.85 g of compound 2

(2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0256 moles of compound per mole of silver and 369 mg of compound per square meter of coated film. The results are reported in the following Table 3.

TABLE 3

Sample	Compound	Contaminant Amount (mmol/m2/side)	ΔD%
7 (C)	-	0.06	- 6.0
8 (I)	3	0.06	- 1.2
9 (I)	3	0.06	- 1.8
10 (I)	3	0.06	- 1.2
11 (I)	2	0.06	- 1.2
12 (I)	2	0.06	- 2.3
13 (I)	2	0.06	- 0.6

[0095] The control sample 7 shows the desensitization effect of 0.06 millimole per square meter of iron (III) on our system. The data of invention samples 8 to 13 clearly show that the aryl compounds described in the present invention are able to reduce the negative effect of iron (III).

Example 4

Sample 14 (Control)

[0096] The procedure of sample 1 is repeated, except that the film sample is subjected to iron (III) contamination using 23 ml per square meter of a solution containing 0.1% by weight ferric sulfate $Fe_2(SO_4)_3$ as iron source, 1% of standard gelatin (manufactured by Deutsche Gelatin Fabrik AG, Germany) as coating auxiliary and 0.12% of Triton™ X 100 as surfactant. This solution is coated on half the surface of a 10 by 28 cm sheet with a Mayer bar number ten. The results are reported in the following Table 4.

Sample 15 (Invention)

[0097] The procedure of sample 14 is repeated, except that during addition of coating finals, 2 g of compound 3 (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0064 moles of compound per mole of silver and 83 mg of compound per square meter of coated film. The results are reported in the following Table 4.

Sample 16 (Invention)

[0098] The procedure of sample 14 is repeated, except that during addition of coating finals, 4 g of compound 3 (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0128 moles of compound per mole of silver and 166 mg of compound per square meter of coated film. The results are reported in the following Table 4.

Sample 17 (Invention)

[0099] The procedure of sample 14 is repeated, except that during addition of coating finals, 8 g of compound 3 (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0256 moles of compound per mole of silver and 333 mg of compound per square meter of coated film. The results are reported in the following Table 4.

Sample 18 (Invention)

[0100] The procedure of sample 14 is repeated, except that during addition of coating finals, 2.21 g of compound 2

(2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0064 moles of compound per mole of silver and 92 mg of compound per square meter of coated film. The results are reported in the following Table 4.

Sample 19 (Invention)

[0101] The procedure of sample 14 is repeated, except that during addition of coating finals, 4.42 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0128 moles of compound per mole of silver and 184 mg of compound per square meter of coated film. The results are reported in the following Table 4.

Sample 20 (Invention)

[0102] The procedure of sample 14 is repeated, except that during addition of coating finals, 8.85 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0256 moles of compound per mole of silver and 368 mg of compound per square meter of coated film. The results are reported in the following Table 4.

TABLE 4

Sample	Compound	Contaminant Amount (mmol/m2/side)	ΔD%
14 (C)	-	0.12	- 8.0
15 (I)	3	0.12	- 4.2
16 (I)	3	0.12	- 3.6
17 (I)	3	0.12	- 1.8
18 (I)	2	0.12	- 2.4
19 (I)	2	0.12	- 1.8
20 (I)	2	0.12	- 1.2

[0103] The control sample 14 shows the desensitization effect of 0.12 millimole per square meter of iron (III). The data of invention samples 15 to 20 show the positive effects of the aryl compounds described in the present invention even when the contaminant is present in high proportion with respect to the aryl compounds.

Example 5

Sample 21 (control)

[0104] The procedure of sample 1 is repeated, except that the fresh film sample was kept 3 days at 38°C before being subjected to copper (II) contamination using 11.4 ml per m^2 of a solution containing 0.125% by weight cupric nitrate $Cu(NO_3)_2$ as copper source, 1% standard gelatin (manufactured by Deutsche Gelatin Fabrik AG, Germany) as coating auxiliary, 0.12% of Triton™ X100 as surfactant coated on half the surface of a 10 by 28 cm sheet with a Mayer bar number five. The results are reported in the following Table 5.

Sample 22 (Invention)

[0105] The procedure of sample 21 is repeated, except that during addition of coating finals, 2 g of compound 3 (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0064 moles of compound per mole of silver and 83 mg of compound per square meter of coated film. The results are reported in the following Table 5.

Sample 23 (Invention)

[0106] The procedure of sample 21 is repeated, except that during addition of coating finals, 4 g of compound 3 (4,5-

dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0128 moles of compound per mole of silver and 166 mg of compound per square meter of coated film. The results are reported in the following Table 5.

Sample 24 (Invention)

[0107] The procedure of sample 21 is repeated, except that during addition of coating finals, 8 g of compound 3 (4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt) is added per one mole of silver, corresponding to 0.0256 moles of compound per mole of silver and 333 mg of compound per square meter of coated film. The results are reported in the following Table 5.

Sample 25 (Invention)

[0108] The procedure of sample 21 is repeated, except that during addition of coating finals, 2.21 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0064 moles of compound per mole of silver and 92 mg of compound per square meter of coated film. The results are reported in the following Table 5.

Sample 26 (Invention)

[0109] The procedure of sample 21 is repeated, except that during addition of coating finals, 4.42 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0128 moles of compound per mole of silver and 184 mg of compound per square meter of coated film. The results are reported in the following Table 5.

Sample 27 (Invention)

[0110] The procedure of sample 21 is repeated, except that during addition of coating finals, 8.85 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0256 moles of compound per mole of silver and 368 mg of compound per square meter of coated film. The results are reported in the following Table 5.

TABLE 5

Sample	Compound	Contaminant Amount (mmol/m2/side)	ΔD%
21 (C)	-	0.48	- 10.0
22 (I)	3	0.48	- 3.9
23 (I)	3	0.48	0
24 (I)	3	0.48	- 1.7
25 (I)	2	0.48	- 3.5
26 (I)	2	0.48	- 4.3
27 (I)	2	0.48	- 4.2

[0111] The control sample 21 shows the desensitization effect of 0.48 millimole per square meter of copper (II). The results of samples 22 to 27 clearly show that the aryl compounds described in the present invention are able to reduce the negative effect of copper (II).

Example 6

Sample 28 (Control)

[0112] The procedure of sample 1 was repeated, except that the emulsion was coated on the two faces of a contaminated 7 mil blue polyester base. The contamination was produced during the base manufacturing process by fine metallic iron and copper particles

[0113] Additionally, the fresh film sample was kept 3 days at 38°C before having been exposed to white light with a standard bromograph for 3/10 of second with filter number 5.

[0114] A microscopic examination of the developed material allowed the determination of the number of spot defects present on the film. These defects were counted on 6 sheet samples of 10 by 28 cm and reported as average for one sheet. The results are reported in table 6.

Sample 29 (Invention)

[0115] The procedure of sample 28 was repeated, except that during addition of coating finals, 1.895 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.00548 moles of compound per mole of silver and 78.9 mg of compound per square meter of coated film. The results are reported in the following Table 6.

Sample 30 (Invention)

[0116] The procedure of sample 28 was repeated, except that during addition of coating finals, 3.771 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0109 moles of compound per mole of silver and 157 mg of compound per square meter of coated film. The results are reported in the following Table 6.

Sample 31 (Invention)

[0117] The procedure of sample 28 was repeated, except that during addition of coating finals, 7.543 g of compound 2 (2,5-dihydroxy-1,4-benzenedisulfonic acid dipotassium salt) is added per one mole of silver, corresponding to 0.0218 moles of compound per mole of silver and 314 mg of compound per square meter of coated film. The results are reported in the following Table 6.

TABLE 6

Sample	Compound	Contaminant	Spot Number
28 (C)	-	Fe + Cu	224
29 (I)	2	Fe + Cu	16
30 (I)	2	Fe + Cu	8
31 (I)	2	Fe + Cu	18

[0118] The control sample 28 shows a high number of spot defects due to iron and copper contamination during base preparation. The invention samples 29 to 31 clearly show that the aryl compounds described in the present invention are able to drastically reduce the number of defects. So, these compounds are able to efficiently prevent the formation of spot defects on a film prepared with a very highly contaminated base.

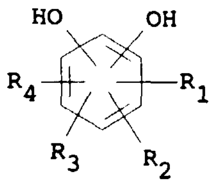
Claims

1. A process for the manufacture of a silver halide element comprising the steps in the following order of:

    (a) making a silver halide emulsion,
    (b) sensitizing said silver halide emulsion either chemically or optically, and
    (c) coating said silver halide emulsion onto a support base,

    characterized in that said process further comprises the step of adding to said silver halide emulsion before the coating step (c), an aryl compound having at least two hydroxyl groups and at least one additional substituent represented by a sulfonic group, an hydroxyl group, a carboxy group or an hydroxymethyl group in an amount of less than 0.03 moles per mole of silver.

2. The process according to claim 1, wherein said aryl compound is represented by the following formula:



wherein R_1 to R_4 are selected from the group consisting of a hydrogen atom, a sulfonic group, an hydroxyl group, a carboxy group and an hydroxymethyl group, provided that at least one of R_1 to R_4 is different from hydrogen atom.

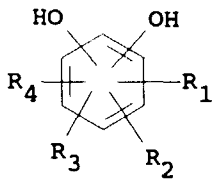
3. The process according to claim 1, wherein said aryl compound is added in an amount of from 0.0001 to 0.03 moles per mole of silver.

4. The process according to claim 1, wherein said aryl compound is added in an amount of from 0.005 to 0.03 moles per mole of silver.

5. The process according to claim 1, wherein said silver halide emulsion is a tabular grain silver halide emulsion having an aspect ratio of at least 2:1.

6. The use of an aryl compound having at least two hydroxyl groups and at least one additional substituent represented by a sulfonic group, an hydroxyl group, a carboxy group or an hydroxymethyl group to eliminate spot defects due to metallic contamination of a silver halide photographic emulsion comprising silver halide tabular grains.

7. The use according to claim 6 wherein said aryl compound is represented by the following formula:

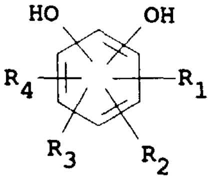


wherein R_1 to R_4 are selected from the group consisting of a hydrogen atom, a sulfonic group, an hydroxyl group, a carboxy group and an hydroxymethyl group, provided that at least one of R_1 to R_4 is different from hydrogen atom.

8. A metal-contaminate free silver halide emulsion characterized in that said silver halide emulsion comprises an aryl compound having at least two hydroxyl groups and at least one additional substituent represented by a sulfonic group, an hydroxyl group, a carboxy group or an hydroxymethyl group in an amount of less than 0.03 moles per mole of silver.

9. A silver halide photographic element comprising a support base having coated thereon at least one silver halide emulsion layer, characterized in that said silver halide emulsion layer comprises an aryl compound having at least two hydroxyl groups and at least one additional substituent represented by a sulfonic group, an hydroxyl group, a carboxy group or an hydroxymethyl group in an amount of less than 0.03 moles per mole of silver.

10. The silver halide photographic element according to claim 9 wherein said aryl compound is represented by the following formula:



wherein R_1 to R_4 are selected from the group consisting of a hydrogen atom, a sulfonic group, an hydroxyl group, a carboxy group and an hydroxymethyl group, provided that at least one of R_1 to R_4 is different from hydrogen atom.

11. The silver halide photographic element according to claim 9, wherein said silver halide emulsion is a tabular grain silver halide emulsion having an aspect ratio of at least 2:1.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 6342

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y	US 3 236 652 A (KENNARD ET AL.) 22 February 1966 * the whole document *	1-4,6-10 5,11	G03C1/34 G03C1/33
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TECHNICAL FIELDS SEARCHED (Int.Cl.6)
G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 June 1998	Buscha, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons

& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 97 11 6342

15-06-1998

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