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(54) **Low silver color photographic element and process for dye image formation**

Farbphotographisches Element mit niedrigem Silbergehalt und Verfahren zur Farbbildherstellung

Élément photographique en couleurs à basse teneur d'argent et procédé de formation d'une image
en couleurs

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Description

[0001] The invention is directed color photographic elements containing silver halide emulsions and to processes for producing dye images.

5 [0002] Radiation sensitive silver halide emulsions containing one or a combination of chloride, bromide and iodide ions have been long recognized to be useful in photography. Each halide ion selection is known to impart particular photographic advantages. By a wide margin the most commonly employed photographic emulsions are silver bromide and bromiodide emulsions. Although known and used for many years for selected photographic applications, the more rapid developability and the ecological advantages of high chloride emulsions have provided an impetus for
10 employing these emulsions over a broader range of photographic applications. As employed herein the term "high chloride emulsion" refers to a silver halide emulsion containing at least 50 mole percent chloride, based on total silver. The most ecologically attractive high chloride emulsions are those that contain very low levels of iodide ion.

[0003] During the 1980's a marked advance took place in silver halide photography based on the discovery that a wide range of photographic advantages, such as improved speed-granularity relationships, increased covering power both on an absolute basis and as a function of binder hardening, more rapid developability, increased thermal stability, increased separation of native and spectral sensitization imparted imaging speeds, and improved image sharpness in
15 both mono- and multi-emulsion layer formats, can be realized by increasing the proportions of selected tabular grain populations in photographic emulsions.

[0004] Although varied definitions have been adopted in defining tabular grain emulsions, there is a general consensus that the functionally significant distinguishing feature of tabular grains lies in the disparity between tabular grain equivalent circular diameter (**ECD**, the diameter of a circle having an area equal to the projected area of the tabular grain) and tabular grain thickness (**t**, the dimension of the tabular grain normal to its opposed parallel major faces). Tabular grain aspect ratio (**ECD/t**) is an art accepted quantifier of this disparity. To distinguish tabular grain emulsions from those that contain only incidental tabular grain inclusions it is also the recognized practice of the art to require
20 that a significant percentage (e.g., greater than 30 percent and more typically greater than 50 percent) of total grain projected area be accounted for by tabular grains having an aspect ratio of at least 2 and more typically an average aspect ratio of at least 5.

[0005] In almost every instance tabular grain emulsions satisfying grain thickness (**t**), aspect ratio (**ECD/t**), and projected area aims have been formed by introducing two or more parallel twin planes into octahedral grains during their preparation. Regular octahedral grains are bounded by {111} crystal faces. The predominant feature of tabular grains formed by twinning are opposed parallel {111} major crystal faces. The major crystal faces have a three fold symmetry, typically appearing triangular or hexagonal.

[0006] The formation of tabular grain emulsions containing parallel twin planes is most easily accomplished in the preparation of silver bromide emulsions. The art has developed the capability of including photographically useful levels of iodide. The inclusion of high levels of chloride as opposed to bromide, alone or in combination with iodide, has been difficult. Silver chloride differs from silver bromide in exhibiting a much stronger propensity toward the formation of grains with faces lying in {100} crystallographic planes. Unfortunately, twinning of grains bounded by {100} crystal faces does not produce grains having a tabular shape. To produce successfully a high chloride tabular grain emulsion by twinning, conditions must be found that favor both the formation of twin planes and {111} crystal faces. Further, after
30 the emulsion has been formed, care in subsequent handling must be exercised to avoid reversion of the grains to their favored more stable form exhibiting {100} crystal faces.

[0007] The following represent background teachings pertinent to emulsions: Wey U.S. Patent 4,399,215, Wey et al U.S. Patent 4,414,306, Maskasky U.S. Patent 4,400,463 (hereinafter designated Maskasky I), Maskasky U.S. Patent 4,713,323 (hereinafter designated Maskasky II), King et al U.S. Patent 4,942,120), Tufano et al U.S. Patent 4,804,621, Takada et al U.S. Patent 4,783,398, Nishikawa et al U.S. Patent 4,952,491, Ishiguro et al U.S. Patent 4,983,508, Bogg U.S. Patent 4,063,951, Mignot U.S. Patent 4,386,156, EP-A-0 584 815 and EP-A-0 534 395, both documents do not belong to the state-of-the-art by virtue of Article 54(2)EPC, disclose high chloride tabular grain emulsions, wherein the grains exhibit {100} crystal faces.

[0008] From time to time interest has been expressed in redox amplification processing to produce dye images in color photographic elements containing silver halide emulsions. The principal advantage of redox amplification processing is that lower silver coverages can be employed in construction of the color photographic elements. Redox amplification processing and color photographic elements particularly structured for such processing are disclosed by *Research Disclosure*, Vol. 308, December 1989, Item 308119, Section XIX, Sub-sections G and H. *Research Disclosure* is published by Kenneth Mason Publications, Ltd., Dudley House, 12 North St., Emsworth, Hampshire P010 7DQ, England.
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[0009] In attempting to combine the known advantages of high aspect ratio tabular grain emulsions, high chloride emulsions and redox amplification processing a problem has arisen. High chloride silver halide grains prefer grain forms having {100} crystallographic faces--e.g., cubic and, less commonly, cubo-octahedral forms. Prior to the present
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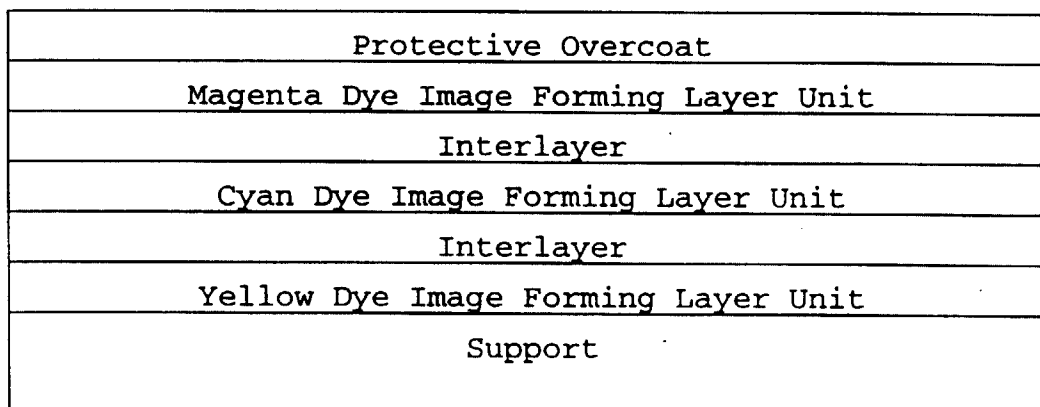
invention in those instances in which redox amplification processing has been undertaken employing high chloride emulsions the grains have typically been high chloride cubic grains.

[0010] In one aspect the present invention is directed to a color photographic element containing a dye image forming layer unit comprised of at least one silver halide emulsion and a dye image providing compound characterized in that total silver in the dye image forming layer unit is less than 200 mg/m² and the emulsion contains a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population, and greater than 30 percent of the grain population projected area is accounted for by tabular grains each having an aspect ratio of at least 2, a mean thickness of less than 0.3 μm, and parallel major faces lying in {100} crystallographic planes.

[0011] In another aspect this invention is directed to a process of producing a dye image in an imagewise exposed color photographic element, containing a dye image forming layer unit comprised of at least one silver halide emulsion and a dye image providing compound, by developing the silver halide emulsion to produce silver imagewise and employing the developed silver to catalyze the reaction of an oxidizing agent and a reducing agent that are inert to oxidation-reduction interaction in the absence of developed silver, and reacting oxidized reducing agent with the dye image providing compound to form the dye image, characterized in that total silver in the dye image forming layer units is less than 200 mg/m² and the emulsion contains a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population, and greater than 30 percent of the grain population projected area is accounted for by tabular grains each having an aspect ratio of at least 2, a mean thickness of less than 0.3 μm, and parallel major faces lying in {100} crystallographic planes.

[0012] The present invention offers a combination of advantages not previously realized. Employing tabular grain emulsions realizes the known advantages, including improved sensitivity and increased image sharpness of these emulsions. By employing high aspect ratio tabular grains that are high chloride grains the advantages of more rapid processing and improved environmental compatibility of spent processing solutions are realized. By employing high chloride tabular grains having major faces lying in {100} crystallographic planes tabular grains (hereinafter referred to as {100} tabular grains) have been provided that are inherently more stable than {111} tabular grains. For example, the {100} tabular grains show no tendency to revert to nontabular forms, thereby eliminating any necessity of resorting to adsorbed grain shape stabilizers employed in combination with high chloride {111} tabular grains. When color photographic elements are constructed according to the invention the extremely low levels of total silver typical of redox amplification processing can be combined with the remaining advantages to achieve color photographic elements and redox amplification processing and systems that are superior to those that have heretofore been available within the art. The color photographic elements of the invention have the capability of producing dye images with lower levels of granularity than have heretofore been realized in producing dye images by redox amplification imaging using high chloride emulsions. The color photographic elements also have the capability of producing dye images of conventional quality employing lower levels of total silver than have been employed using high chloride emulsions. Finally, despite the known higher covering power of tabular grains, the color photographic elements can be employed to form retained dye images without bleaching. This offers advantages in silver coverages, in simplifying processing and in improving the environmental compatibility of spent processing solutions.

[0013] In a simple form a color photographic element satisfying the requirements of the invention can be constructed as follows:



Structure I

[0014] The support (S) can be either a transmissive or reflective support and can take any conventional form, such as any of the forms disclosed in *Research Disclosure*, Item 308119, cited above, Section XVII. When the color photo-

graphic element is employed as a camera film, the support is preferably a transparent film support, preferably provided with a processing solution removable or decolorizable antihalation backing layer, not shown. When the color photographic element is employed to produce a viewable positive image, the support is preferably a reflective support of the type found in a conventional photographic print.

5 [0015] The protective overcoat (OC) is a preferred, but non-essential feature provided to protect physically the underlying layer units from physical damage during handling and processing. The protective overcoat is a transparent layer preferably constructed of a photographic vehicle of type disclosed in *Research Disclosure*, Item 308119, cited above, Section IX, and typically contains one or more of the following: coating aids, such as those disclosed in Section XI; plasticizers and/or lubricants, such as those disclosed in Section XII; antistatic agents, such as those disclosed in 10 Section XIII; and matting agents, such as those disclosed in Section XVI.

[0016] The magenta (M) dye image forming layer unit is coated farthest from the support to receive first imagewise exposing light. The magenta dye image forming layer unit contains at least one silver halide emulsion. The emulsion is most typically a green sensitized emulsion and preferably contains high chloride grains to minimize blue light contamination of the record of green light exposure formed by this emulsion layer.

15 [0017] The cyan (C) dye image forming layer unit is located to receive imagewise exposing light after it has passed through the magenta dye image forming layer unit. The emulsion is most typically a red sensitized emulsion and preferably contains high chloride grains to minimize blue light contamination of the record of red light exposure formed by this emulsion layer.

20 [0018] The yellow (Y) dye image forming layer unit is typically blue-sensitized and is coated nearest the support, since the human eye is least sensitive to this image. Hence the lower image sharpness during exposure received by this dye image forming layer unit afforded by this coating location can be best accommodated with less perceived image degradation. The yellow dye image forming layer unit record preferably contains high chloride grains, but for an entirely different reason than the remaining dye image forming layer units. Since processing solutions must penetrate both of the overlying dye image forming layer units to reach the yellow dye image forming layer unit, the selection of 25 high chloride grains, which can be processed more rapidly, for this layer unit offsets this disadvantage. Blue sensitization is relied upon to offset the low native blue sensitivity of the high chloride grains in the yellow dye image forming layer unit.

[0019] While it is possible to introduce magenta, cyan and yellow dye image providing compounds in the layer units M, C and Y, respectively, during processing following imagewise exposure, it is preferred to simplify processing by incorporating the dye image providing compounds in the layer units as initially coated. Each dye image providing 30 compound can be blended with the emulsion or emulsions within the layer unit or coated in a contiguously adjacent layer.

[0020] While Structure I, which employs the sequence M/C/Y/S, is preferred, the alternative sequences C/M/Y/S, Y/M/C/S, Y/C/M/S, M/Y/C/S and C/Y/M/S are entirely feasible and contemplated.

35 [0021] The interlayers (IL) contain conventional oxidized developing agent scavengers to prevent inter-unit migration of oxidized developing agent during process that would otherwise produce color contamination of the layer unit dye images. In coating sequences M/C/Y/S and C/M/Y/S conventional yellow filter materials are necessarily absent from the interlayers, but in the remaining coating sequences yellow filter materials can be present in any inter-layer underlying the blue sensitized dye image forming layer unit.

40 [0022] The six dye image forming layer unit sequences described above are exemplary of numerous known dye image forming layer unit sequences. Kofron et al U.S. Patent 4,439,520 discloses a variety of dye image forming layer unit sequences made possible by providing plural dye image layer units responsive to the same region of the spectrum.

[0023] Numerous other variations in construction are possible. Instead of sensitizing the yellow, magenta and cyan dye image forming layer units to blue, green and red light, respectively, one or any combination of the dye image forming layer units can be sensitized to a different portion of the spectrum, including one or more portions of the spectrum that lie outside the visible--e.g., the near ultraviolet and the near infrared.

45 [0024] For replicating the colors of photographic subjects at least three dye image forming layer units are required. However, for specific photographic applications only two or even one dye image forming layer unit is sufficient to provide the dye image required. For example, for forming color separation images a single dye image forming layer unit per element is sufficient. For the simplest multicolor imaging at least two dye image forming layer units are required.

50 [0025] When the photographic element contains at least two and preferably three dye image forming layer units, the color photographic elements of the invention contain less than 400 mg/m² of total silver, preferably less than 220 mg/m² and optimally less than 170 mg/m². Each dye image forming layer unit, whether employed singly or in combination, contains less than 200 mg/m² of total silver, preferably less than 133 mg/m², most preferably less than 110 mg/m² and optimally less than 85 mg/m². When the color photographic elements contain at least two and preferably three dye image forming layer units, the photographic elements preferably contain at least 30 mg/m² total silver and most preferably 55 at least 40 mg/m² total silver. When the color photographic elements contain a reduced number of dye image forming layer units, the total silver in the color photographic element can be proportionately reduced. For example, in a single dye image forming layer unit a minimum of 1 mg/m² of silver is preferred, a minimum of 10 mg/m² of silver is most preferred and a minimum of at least 20 mg/m² of silver is generally optimum.

[0026] The color photographic elements of the invention contain at least one high chloride {100} tabular grain emulsion in at least one dye image forming layer unit. Preferably a high chloride {100} tabular grain emulsion is present in each dye image forming layer unit, and optimally each of the emulsions is a high chloride {100} tabular grain emulsion. When less than all of the emulsions present in the color photographic elements of the invention are high chloride high aspect ratio {100} tabular grain emulsions, the remaining emulsions can take any conventional form known to be useful in redox amplification imaging. In a specifically preferred form they are high chloride cubic or cubo-octahedral grain emulsions. In an alternative specifically contemplated form they are tabular grain silver bromide or iodobromide emulsions. It is also possible to employ high chloride {100} tabular grain emulsions in combination with high chloride {111} tabular grain emulsions; however, since high chloride {100} tabular grain emulsions can satisfy the same application requirements as high chloride {111} tabular grain emulsions and offer the additional advantage of inherent grain shape stability, it is specifically preferred that all high chloride tabular grain emulsions employed be high chloride {100} tabular grain emulsions. The incorporation of blended emulsions in the dye image forming layer units is specifically contemplated to achieve known adjustments of imaging characteristics. It is, however, generally preferred that the high chloride emulsion or emulsions present in a dye image forming layer be the sole latent image forming emulsion or emulsions present.

[0027] The high chloride {100} tabular grain emulsions incorporated within the color photographic elements and in the processes of the invention each contain a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population, and greater than 30 percent of the grain population projected area is accounted for by tabular grains each having an aspect ratio of at least 2, a thickness of less than 0.3 μm , and parallel major faces lying in {100} crystallographic planes.

[0028] It is generally preferred that the highest conveniently attainable proportion of total grain projected area be accounted for by high chloride {100} tabular grains having an aspect ratio of at least 2 and a thickness of less than 0.3 μm , hereinafter referred to as the selected high chloride {100} tabular grain population. The selected high chloride {100} tabular grain population preferably accounts for at least 50 percent, most preferably at least 70 percent and optimally at least 90 percent of the total high chloride grain population present within a dye image forming layer unit.

[0029] Acicular and rod-like grains with {100} major faces are, of course, excluded in arriving at the above selected high chloride {100} tabular grain projected areas. Typically such grains constitute a negligibly small fraction of the total grain population. In those rare instances in which the presence of rod-like {100} is not negligibly small discrimination between rods and rod-like grains and tabular grains is readily accomplished by visual inspection of photomicrographs, and, for the purpose of providing a quantitative demarcation, rectangular grains, indicative of a {100} grain face, having a ratio of adjacent edge lengths of 10 or greater are excluded from the selected high chloride {100} tabular grain population.

[0030] The selected high chloride {100} tabular grain population preferably exhibits an average aspect ratio of at least 5 and most preferably at least 8. By considering that the maximum useful average ECD of a photographic emulsion is about 10 μm , it is apparent that as a tabular grain thickness of just less than 0.3 μm the average aspect ratio of the tabular grains just exceeds 33.3. When the high chloride {100} tabular grains are selected on the basis of a preferred thickness of less than 0.2 μm (the thickness criterion for thin tabular grains), the average aspect ratio rises to greater than 50. With an optimum tabular grain thickness of less than 0.1 μm average aspect ratios can range in excess of 100. Depending upon the emulsion preparation procedure employed extremely thin high chloride {100} tabular grains can form the selected tabular grain population. Ultrathin, less than 0.07 μm in thickness, high chloride {100} tabular grain populations satisfying the above projected areas can be prepared. In actual practice, maximum average ECD's rarely exceed 6 μm and more commonly are less than 4 μm . Hence average aspect ratios of from 5 to 100 and more commonly from 8 to 50 are typical of the selected high chloride {100} tabular grain populations contemplated for use in the practice of the invention.

[0031] In one preferred form the high chloride {100} tabular grain emulsions containing at least 50 mole percent chloride and less than 2 mole percent iodide, with any remaining halide being bromide. Silver chloride, iodochloride, bromochloride, iodobromochloride and bromiodochloride emulsions are specifically contemplated. In one specifically preferred form the high chloride {100} tabular grains are internally free of iodide and most preferably internally free of iodide at the grain nucleation site. When the grains are nucleated in the absence of iodide, pure silver chloride {100} tabular grains can be produced. Emulsions of this type can be produced by the precipitation techniques taught by Maskasky U.S. Patent 5,264,337, cited above. Further descriptions of the preparation of emulsions of this type are provided in the examples and in the discussion that follows.

[0032] An alternative approach is to nucleate the high chloride {100} tabular grains in the presence of iodide. In this process grain nucleation occurs in a high chloride environment in the presence of iodide ion under conditions that favor the emergence of {100} crystal faces. As grain formation occurs the inclusion of iodide into the cubic crystal lattice being formed by silver ions and the remaining halide ions is disruptive because of the much larger diameter of iodide ion as compared to chloride ion. The incorporated iodide ions introduce crystal irregularities that in the course of further grain growth result in tabular grains rather than regular (cubic) grains.

[0033] It is believed that at the outset of nucleation the incorporation of iodide ion into the crystal structure results in cubic grain nuclei being formed having one or more growth accelerating irregularities in one or more of the cubic crystal faces. The cubic crystal faces that contain at least one irregularity thereafter accept silver halide at an accelerated rate as compared to the regular cubic crystal faces (i.e., those lacking an irregularity). When only one of the cubic crystal faces contains an irregularity, grain growth on only one face is accelerated, and the resulting grain structure on continued growth is a rod. The same result occurs when only two opposite parallel faces of the cubic crystal structure contain irregularities. However, when any two contiguous cubic crystal faces contain an irregularity, continued growth accelerates growth on both faces and produces a tabular grain structure. It is believed that the tabular grains of the emulsions are produced by those grain nuclei having two, three or four faces containing growth accelerating irregularities.

[0034] At the outset of precipitation a reaction vessel is provided containing a dispersing medium and conventional silver and reference electrodes for monitoring halide ion concentrations within the dispersing medium. Halide ion is introduced into the dispersing medium that is at least 50 mole percent chloride--i.e., at least half by number of the halide ions in the dispersing medium are chloride ions. The pCl of the dispersing medium is adjusted to favor the formation of {100} grain faces on nucleation--that is, within the range of from 0.5 to 3.5, preferably within the range of from 1.0 to 3.0 and, optimally, within the range of from 1.5 to 2.5.

[0035] The grain nucleation step is initiated when a silver jet is opened to introduce silver ion into the dispersing medium. Iodide ion is preferably introduced into the dispersing medium concurrently with or, optimally, before opening the silver jet. Effective tabular grain formation can occur over a wide range of iodide ion concentrations ranging up to the saturation limit of iodide in silver chloride. The saturation limit of iodide in silver chloride is reported by H. Hirsch, "Photographic Emulsion Grains with Cores: Part I. Evidence for the Presence of Cores", *J. of Photog. Science*, Vol. 10 (1962), pp. 129-134, to be 13 mole percent. In silver halide grains in which equal molar proportions of chloride and bromide ion are present up to 27 mole percent iodide, based on silver, can be incorporated in the grains. It is preferred to undertake grain nucleation and growth below the iodide saturation limit to avoid the precipitation of a separate silver iodide phase and thereby avoid creating an additional category of unwanted grains. It is generally preferred to maintain the iodide ion concentration in the dispersing medium at the outset of nucleation at less than 10 mole percent. In fact, only minute amounts of iodide at nucleation are required to achieve the desired tabular grain population. Initial iodide ion concentrations of down to 0.001 mole percent are contemplated. However, for convenience in replication of results, it is preferred to maintain initial iodide concentrations of at least 0.01 mole percent and, optimally, at least 0.05 mole percent.

[0036] In a preferred method, silver iodochloride grain nuclei are formed during the nucleation step. Minor amounts of bromide ion can be present in the dispersing medium during nucleation. Any amount of bromide ion can be present in the dispersing medium during nucleation that is compatible with at least 50 mole percent of the halide in the grain nuclei being chloride ions. The grain nuclei preferably contain at least 70 mole percent and optimally at least 90 mole percent chloride ion, based on silver.

[0037] Grain nuclei formation occurs instantaneously upon introducing silver ion into the dispersing medium. For manipulative convenience and reproducibility, silver ion introduction during the nucleation step is preferably extended for a convenient period, typically from 5 seconds to less than a minute. So long as the pCl remains within the ranges set forth above no additional chloride ion need be added to the dispersing medium during the nucleation step. It is, however, preferred to introduce both silver and halide salts concurrently during the nucleation step. The advantage of adding halide salts concurrently with silver salt throughout the nucleation step is that this permits assurance that any grain nuclei formed after the outset of silver ion addition are of essentially similar halide content as those grain nuclei initially formed. Iodide ion addition during the nucleation step is particularly preferred. Since the deposition rate of iodide ion far exceeds that of the other halides, iodide will be depleted from the dispersing medium unless replenished.

[0038] Any convenient conventional source of silver and halide ions can be employed during the nucleation step. Silver ion is preferably introduced as an aqueous silver salt solution, such as a silver nitrate solution. Halide ion is preferably introduced as alkali or alkaline earth halide, such as lithium, sodium and/or potassium chloride, bromide and/or iodide.

[0039] It is possible, but not preferred, to introduce silver chloride or silver iodochloride Lippmann grains into the dispersing medium during the nucleation step. In this instance grain nucleation has already occurred and what is referred to hereinbefore as the nucleation step is in reality a step for introduction of grain facet irregularities. The disadvantage of delaying the introduction of grain facet irregularities is that this produces thicker tabular grains than would otherwise be obtained.

[0040] The dispersing medium contained in the reaction vessel prior to the nucleation step is comprised of water, the dissolved halide ions discussed above and a peptizer. The dispersing medium can exhibit a pH within any convenient conventional range for silver halide precipitation, typically from 2 to 8. It is preferred, but not required, to maintain the pH of the dispersing medium on the acid side of neutrality (i.e., < 7.0). To minimize fog a preferred pH range for precipitation is from 2.0 to 5.0. Mineral acids, such as nitric acid or hydrochloric acid, and bases, such as alkali

hydroxides, can be used to adjust the pH of the dispersing medium. It is also possible to incorporate pH buffers.

[0041] The peptizer can take any convenient conventional form known to be useful in the precipitation of photographic silver halide emulsions and particularly tabular grain silver halide emulsions. A summary of conventional peptizers is provided in *Research Disclosure*, Item 308119, cited above, Section IX. While synthetic polymeric peptizers of the type disclosed by Maskasky I, cited above and here incorporated by reference, can be employed, it is preferred to employ gelatino peptizers (e.g., gelatin and gelatin derivatives). As manufactured and employed in photography gelatino peptizers typically contain significant concentrations of calcium ion, although the use of deionized gelatino peptizers is a known practice. In the latter instance it is preferred to compensate for calcium ion removal by adding divalent or trivalent metal ions, such as alkaline earth or earth metal ions, preferably magnesium, calcium, barium or aluminum ions. Specifically preferred peptizers are low methionine gelatino peptizers (i.e., those containing less than 30 micromoles of methionine per gram of peptizer), optimally less than 12 micromoles of methionine per gram of peptizer. These peptizers and their preparation are described by Maskasky II and King et al, cited previously. However, it should be noted that the grain growth modifiers of the type taught for inclusion in the emulsions of Maskasky I and II (e.g., adenine) are not appropriate for inclusion in the dispersing media, since these grain growth modifiers promote twinning and the formation of tabular grains having {111} major faces. Generally at least about 10 percent and typically from 20 to 80 percent of the dispersing medium forming the completed emulsion is present in the reaction vessel at the outset of the nucleation step. It is conventional practice to maintain relatively low levels of peptizer, typically from 10 to 20 percent of the peptizer present in the completed emulsion, in the reaction vessel at the start of precipitation. To increase the proportion of thin tabular grains having {100} faces formed during nucleation it is preferred that the concentration of the peptizer in the dispersing medium be in the range of from 0.5 to 6 percent by weight of the total weight of the dispersing medium at the outset of the nucleation step. It is conventional practice to add gelatin, gelatin derivatives and other vehicles and vehicle extenders to prepare emulsions for coating after precipitation. Any naturally occurring level of methionine can be present in gelatin and gelatin derivatives added after precipitation is complete.

[0042] The nucleation step can be performed at any convenient conventional temperature for the precipitation of silver halide emulsions. Temperatures ranging from near ambient--e.g., 30°C up to about 90°C are contemplated, with nucleation temperatures in the range of from 35 to 70°C being preferred.

[0043] Since grain nuclei formation occurs almost instantaneously, only a very small proportion of the total silver need be introduced into the reaction vessel during the nucleation step. Typically from about 0.1 to 10 mole percent of total silver is introduced during the nucleation step.

[0044] A grain growth step follows the nucleation step in which the grain nuclei are grown until tabular grains having {100} major faces of a desired average ECD are obtained. Whereas the objective of the nucleation step is to form a grain population having the desired incorporated crystal structure irregularities, the objective of the growth step is to deposit additional silver halide onto (grow) the existing grain population while avoiding or minimizing the formation of additional grains. If additional grains are formed during the growth step, the polydispersity of the emulsion is increased and, unless conditions in the reaction vessel are maintained as described above for the nucleation step, the additional grain population formed in the growth step will not have the desired tabular grain properties described herein for use in the invention.

[0045] In its simplest form the process of preparing emulsions can be performed as a single jet precipitation without interrupting silver ion introduction from start to finish. As is generally recognized by those skilled in the art a spontaneous transition from grain formation to grain growth occurs even with an invariant rate of silver ion introduction, since the increasing size of the grain nuclei increases the rate at which they can accept silver and halide ion from the dispersing medium until a point is reached at which they are accepting silver and halide ions at a sufficiently rapid rate that no new grains can form. Although manipulatively simple, single jet precipitation limits halide content and profiles and generally results in more polydisperse grain populations.

[0046] It is usually preferred to prepare photographic emulsions with the most geometrically uniform grain populations attainable, since this allows a higher percentage of the grain population to be optimally sensitized and otherwise optimally prepared for photographic use. Further, it is usually more convenient to blend relatively monodisperse emulsions to obtain aim sensitometric profiles than to precipitate a single polydisperse emulsion that conforms to an aim profile.

[0047] In the preparation of the desired emulsions it is preferred to interrupt silver and halide salt introductions at the conclusion of the nucleation step and before proceeding to the growth step that brings the emulsions to their desired final size and shape. The emulsions are held within the temperature ranges described herein for nucleation for a period sufficient to allow reduction in grain dispersity. A holding period can range from a minute to several hours, with typical holding periods ranging from 5 minutes to an hour. During the holding period relatively smaller grain nuclei are Ostwald ripened onto surviving, relatively larger grain nuclei, and the overall result is a reduction in grain dispersity.

[0048] If desired, the rate of ripening can be increased by the presence of a ripening agent in the emulsion during the holding period. A conventional simple approach to accelerating ripening is to increase the halide ion concentration in the dispersing medium. This creates complexes of silver ions with plural halide ions that accelerate ripening. When this approach is employed, it is preferred to increase the chloride ion concentration in the dispersing medium. That is,

it is preferred to lower the pCl of the dispersing medium into a range in which increased silver chloride solubility is observed. Alternatively, ripening can be accelerated and the percentage of the grain population projected area accounted for by {100} tabular grains can be increased by employing conventional ripening agents. Preferred ripening agents are sulfur containing ripening agents, such as thioethers. Typical thioether ripening agents are disclosed by McBride U.S. Patent 3,271,157, Jones U.S. Patent 3,574,628 and Rosencrantz et al U.S. Patent 3,737,313. More recently crown thioethers have been suggested for use as ripening agents. Ripening agents containing a primary or secondary amino moiety, such as imidazole, glycine or a substituted derivative, are also effective. Sodium sulfite has been demonstrated to be effective in increasing the percentage of total grain projected area accounted by the {100} tabular grains.

[0049] Once the desired population of grain nuclei have been formed, grain growth can proceed according to any convenient conventional precipitation technique for the precipitation of silver halide grains bounded by {100} grain faces. Whereas iodide and chloride ions are required to be incorporated into the grains during nucleation and are therefore present in the completed grains at the internal nucleation site, any halide or combination of halides known to form a cubic crystal lattice structure can be employed during the growth step. Neither iodide nor bromide ions need be incorporated in the grains during the growth step, since the irregular grain nuclei faces that result in tabular grain growth, once introduced, persist during subsequent grain growth independently of the halide being precipitated, provided the halide or halide combination is one that forms a cubic crystal lattice. This excludes only iodide levels above 13 mole percent (preferably 6 mole percent) in precipitating silver iodochloride, levels of iodide above 40 mole percent (preferably 30 mole percent) in precipitating silver iodobromide, and proportionally intermediate levels of iodide in precipitating silver iodohalides containing bromide and chloride. When silver bromide or silver iodobromide is being deposited during the growth step, it is preferred to maintain a pBr within the dispersing medium in the range of from 1.0 to 4.2, preferably 1.6 to 3.4. When silver chloride, silver iodochloride, silver bromochloride or silver iodobromochloride is being deposited during the growth step, it is preferred to maintain the pCl within the dispersing medium within the ranges noted above in describing the nucleation step.

[0050] It has been discovered quite unexpectedly that up to 20 percent reductions in tabular grain thicknesses can be realized by specific halide introductions during grain growth. Surprisingly, it has been observed that bromide additions during the growth step in the range of from 0.05 to 15 mole percent, preferably from 1 to 10 mole percent, based on silver, produce relatively thinner {100} tabular grains than can be realized under the same conditions of precipitation in the absence of bromide ion. Similarly, it has been observed that iodide additions during the growth step in the range of from 0.001 to <1 mole percent, based on silver, produce relatively thinner {100} tabular grains than can be realized under the same conditions of precipitation in the absence of iodide ion.

[0051] During the growth step both silver and halide salts are preferably introduced into the dispersing medium. In other words, double jet precipitation is contemplated, with added iodide salt, if any, being introduced with the remaining halide salt or through an independent jet. The rate at which silver and halide salts are introduced is controlled to avoid renucleation--that is, the formation of a new grain population. Addition rate control to avoid renucleation is generally well known in the art, as illustrated by Wilgus German OLS No. 2,107,118, Irie U.S. Patent 3,650,757, Kurz U.S. Patent 3,672,900, Saito U.S. Patent 4,242,445 and Wey "Growth Mechanism of AgBr Crystals in Gelatin Solution", *Photographic Science and Engineering*, Vol. 21, No. 1, Jan./Feb. 1977, p. 14, *et seq.*

[0052] In the simplest form of the grain preparation the nucleation and growth stages of grain precipitation occur in the same reaction vessel. It is, however, recognized that grain precipitation can be interrupted, particularly after completion of the nucleation stage. Further, two separate reaction vessels can be substituted for the single reaction vessel described herein. The nucleation stage of grain preparation can be performed in an upstream reaction vessel (herein also termed a nucleation reaction vessel) and the dispersed grain nuclei can be transferred to a downstream reaction vessel in which the growth stage of grain precipitation occurs (herein also termed a growth reaction vessel). In one arrangement of this type an enclosed nucleation vessel can be employed to receive and mix reactants upstream of the growth reaction vessel, as illustrated by Posse et al U.S. Patent 3,790,386, Forster et al U.S. Patent 3,897,935, Finnicum et al U.S. Patent 4,147,551, and Verhille et al U.S. Patent 4,171,224. In these arrangements the contents of the growth reaction vessel are recirculated to the nucleation reaction vessel.

[0053] It is herein contemplated that various parameters important to the control of grain formation and growth, such as pH, pAg, ripening, temperature, and residence time, can be independently controlled in the separate nucleation and growth reaction vessels. To allow grain nucleation to be entirely independent of grain growth occurring in the growth reaction vessel down stream of the nucleation reaction vessel, no portion of the contents of the growth reaction vessel should be recirculated to the nucleation reaction vessel. Preferred arrangements that separate grain nucleation from the contents of the growth reaction vessel are disclosed by Mignot U.S. Patent 4,334,012 (which also discloses the useful feature of ultrafiltration during grain growth), Urabe U.S. Patent 4,879,208 and published European Patent Applications 326 852, 326 853, 355 535 and 370 116, Ichizo published European Patent Application 368 275, Urabe et al published European Patent Application 374 954, and Onishi et al published Japanese Patent Application (Kokai) 172,817-A (1990).

[0054] Although the process of grain nucleation has been described hereinbefore in terms of utilizing iodide to produce the crystal irregularities required for tabular grain formation, alternative nucleation procedures have been devised, as demonstrated in the following Examples, that eliminate any requirement of iodide ion being present during nucleation in order to produce tabular grains. These alternative procedures are, further, compatible with the use of iodide during nucleation. Thus, these procedures can be relied upon entirely during nucleation for tabular grain formation or can be relied upon in combination with iodide ion during nucleation to produce tabular grains.

[0055] It has been observed that rapid grain nucleations, including so-called dump nucleations, in which significant levels of dispersing medium supersaturated with halide and silver ions exist at nucleation, accelerate introduction of the grain irregularities responsible for tabularity. Since nucleation can be achieved essentially instantaneously, immediate departures from initial supersaturation to the preferred pCl ranges noted herein are entirely consistent with this approach.

[0056] It has also been observed that maintaining the level of peptizer in the dispersing medium during grain nucleation at a level of less than 1 percent by weight enhances tabular grain formation. It is believed that coalescence of grain nuclei pairs can be at least in part responsible for introducing the crystal irregularities that induce tabular grain formation. Limited coalescence can be promoted by withholding peptizer from the dispersing medium or by initially limiting the concentration of peptizer. Mignot U.S. Patent 4,334,012 illustrates grain nucleation in the absence of a peptizer with removal of soluble salt reaction products to avoid coalescence of nuclei. Since limited coalescence of grain nuclei is considered desirable, the active interventions of Mignot to eliminate grain nuclei coalescence can be either eliminated or moderated. It is also contemplated to enhance limited grain coalescence by employing one or more peptizers that exhibit reduced adhesion to grain surfaces. For example, it is generally recognized that low methionine gelatin of the type disclosed by Maskasky II is less tightly absorbed to grain surfaces than gelatin containing higher levels of methionine. Further moderated levels of grain adsorption can be achieved with so-called "synthetic peptizers"--that is, peptizers formed from synthetic polymers. The maximum quantity of peptizer compatible with limited coalescence of grain nuclei is, of course, related to the strength of adsorption to the grain surfaces. Once grain nucleation has been completed, immediately after silver salt introduction, peptizer levels can be increased to any convenient conventional level for the remainder of the precipitation process.

[0057] Dopants, in concentrations of up to 10^{-2} mole per silver mole and typically less than 10^{-4} mole per silver mole, can be present in the grains. Compounds of metals such as copper, thallium, lead, mercury, bismuth, zinc, cadmium, rhenium, and Group VIII metals (e.g., iron, ruthenium, rhodium, palladium, osmium, iridium and platinum) can be present during grain precipitation, preferably during the growth stage of precipitation. The modification of photographic properties is related to the level and location of the dopant within the grains. When the metal forms a part of a coordination complex, such as a hexacoordination complex or a tetracoordination complex, the ligands can also be included within the grains and the ligands can further influence photographic properties. Coordination ligands, such as halo, aquo, cyano cyanate, thiocyanate, nitrosyl, thionitrosyl, oxo and carbonyl ligands are contemplated and can be relied upon to modify photographic properties.

[0058] Dopants and their addition are illustrated by Arnold et al U.S. Patent 1,195,432; Hochstetter U.S. Patent 1,951,933; Trivelli et al U.S. Patent 2,448,060; Overman U.S. Patent 2,628,167; Mueller et al U.S. Patent 2,950,972; McBride U.S. Patent 3,287,136; Sidebotham U.S. Patent 3,488,709; Rosecrants et al U.S. Patent 3,737,313; Spence et al U.S. Patent 3,687,676; Gilman et al U.S. Patent 3,761,267; Shiba et al U.S. Patent 3,790,390; Ohkubo et al U.S. Patent 3,890,154; Iwaosa et al U.S. Patent 3,901,711; Habu et al U.S. Patent 4,173,483; Atwell U.S. Patent 4,269,927; Janusonis et al U.S. Patent 4,835,093; McDugle et al U.S. Patents 4,933,272, 4,981,781, and 5,037,732; Keevert et al U.S. Patent 4,945,035; and Evans et al U.S. Patent 5,024,931. For background as to alternatives known to the art attention is directed to B. H. Carroll, "Iridium Sensitization: A Literature Review", *Photographic Science and Engineering*, Vol. 24, NO. 6, Nov./Dec. 1980, pp. 265-257, and Grzeskowiak et al published European Patent Application 264 288.

[0059] Although not essential, a further procedure that can be employed to maximize the population of high chloride {100} tabular grains is to incorporate an agent capable of restraining the emergence of non-{100} grain crystal faces in the emulsion during its preparation. The restraining agent, when employed, can be active during grain nucleation, during grain growth or throughout precipitation.

[0060] Useful restraining agents under the contemplated conditions of precipitation are organic compounds containing a nitrogen atom with a resonance stabilized π electron pair. Resonance stabilization prevents protonation of the nitrogen atom under the relatively acid conditions of precipitation.

[0061] Aromatic resonance can be relied upon for stabilization of the π electron pair of the nitrogen atom. The nitrogen atom can either be incorporated in an aromatic ring, such as an azole or azine ring, or the nitrogen atom can be a ring substituent of an aromatic ring.

[0062] In one preferred form the restraining agent can satisfy the following formula:

(I)



where

Z represents the atoms necessary to complete a five or six membered aromatic ring structure, preferably formed by carbon and nitrogen ring atoms. Preferred aromatic rings are those that contain one, two or three nitrogen atoms. Specifically contemplated ring structures include 2H-pyrrole, pyrrole, imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, 1,3,5-triazole, pyridine, pyrazine, pyrimidine, and pyridazine.

[0063] When the stabilized nitrogen atom is a ring substituent, preferred compounds satisfy the following formula:

(II)



where

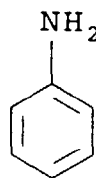
Ar is an aromatic ring structure containing from 5 to 14 carbon atoms and

R¹ and R² are independently hydrogen, Ar, or any convenient aliphatic group or together complete a five or six membered ring.

Ar is preferably a carbocyclic aromatic ring, such as phenyl or naphthyl. Alternatively any of the nitrogen and carbon containing aromatic rings noted above can be attached to the nitrogen atom of formula II through a ring carbon atom. In this instance, the resulting compound satisfies both formulae I and II. Any of a wide variety of aliphatic groups can be selected. The simplest contemplated aliphatic groups are alkyl groups, preferably those containing from 1 to 10 carbon atoms and most preferably from 1 to 6 carbon atoms. Any functional substituent of the alkyl group known to be compatible with silver halide precipitation can be present. It is also contemplated to employ cyclic aliphatic substituents exhibiting 5 or 6 membered rings, such as cycloalkane, cycloalkene and aliphatic heterocyclic rings, such as those containing oxygen and/or nitrogen hetero atoms. Cyclopentyl, cyclohexyl, pyrrolidiny, piperidiny, furanyl and similar heterocyclic rings are specifically contemplated.

[0064] The following are representative of compounds contemplated satisfying formulae I and/or II:

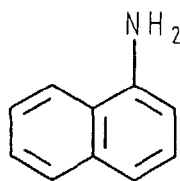
RA-1



aniline

RA-2

5

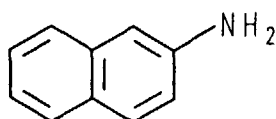


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α-naphthylamine

RA-3

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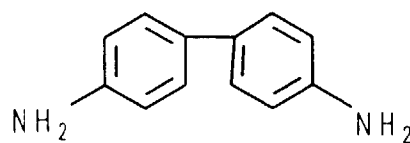


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β-naphthylamine

RA-4

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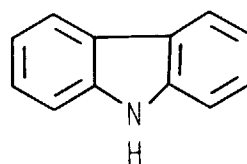


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benzidine

RA-5

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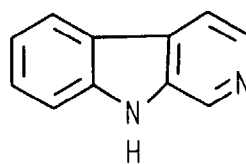


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carbazole

RA-6

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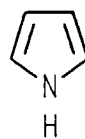


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norharman

RA-7

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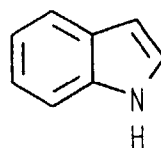


pyrrole

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RA-8

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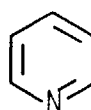


indole

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RA-9

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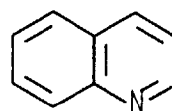


pyridine

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RA-10

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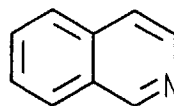


quinoline

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RA-11

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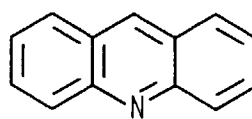
isoquinoline

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RA-12

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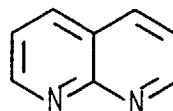


acridine

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RA-13

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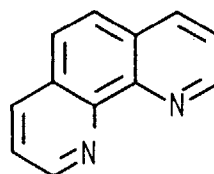


1,8-naphthyridine

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RA-14

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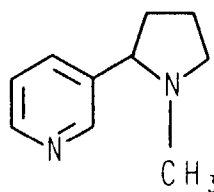
1,10-phenanthroline

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RA-15

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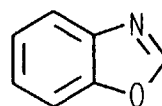


nicotine

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RA-16

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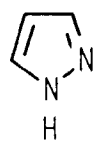


benzoxazole

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RA-17

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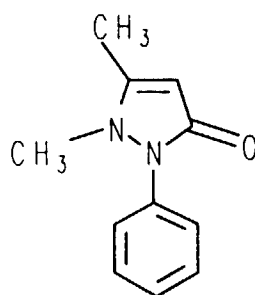


pyrazole

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RA-18

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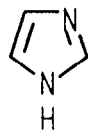
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antipyrine

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RA-19

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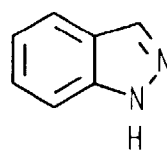
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imidazole

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RA-20

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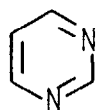
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indazole

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RA-21

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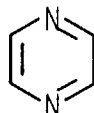


pyrimidine

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RA-22

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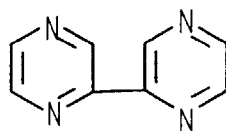


pyrazine

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RA-23

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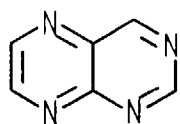


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2,2'-bipyrazine

RA-24

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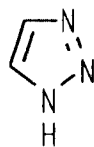
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pteridine

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RA-25

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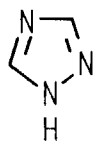


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1,2,3-triazole

RA-26

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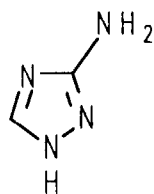


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1,2,4-triazole

RA-27

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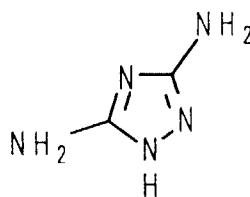


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3-amino-1,2,4-triazole

RA-28

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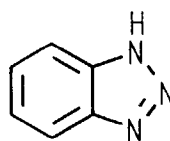
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3,5-diamino-1,2,4-triazole

RA-29

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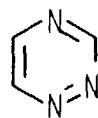
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benzotriazole

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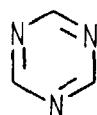
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RA-30



1,2,4-triazine

RA-31



1,3,5-triazine

[0065] Selection of preferred restraining agents and their useful concentrations can be accomplished by the following selection procedure: The compound being considered for use as a restraining agent is added to a silver chloride emulsion consisting essentially of cubic grains with a mean grain edge length of 0.3 μm . The emulsion is 0.2 M in sodium acetate, has a pCl of 2.1, and has a pH that is at least one unit greater than the pKa of the compound being considered. The emulsion is held at 75°C with the restraining agent present for 24 hours. If, upon microscopic examination after 24 hours, the cubic grains have sharper edges of the {100} crystal faces than a control differing only in lacking the compound being considered, the compound introduced is performing the function of a restraining agent. The significance of sharper edges of intersection of the {100} crystal faces lies in the fact that grain edges are the most active sites on the grains in terms of ions reentering the dispersing medium. By maintaining sharp edges the restraining agent is acting to restrain the emergence of non-{100} crystal faces, such as are present, for example, at rounded edges and corners. In some instances instead of dissolved silver chloride depositing exclusively onto the edges of the cubic grains a new population of grains bounded by {100} crystal faces is formed. Optimum restraining agent activity occurs when the new grain population is a tabular grain population in which the tabular grains are bounded by {100} major crystal faces.

[0066] It is specifically contemplated to deposit epitaxially silver salt onto the tabular grains acting as hosts. Conventional epitaxial depositions onto high chloride silver halide grains are illustrated by Maskasky U.S. Patent 4,435,501 (particularly Example 24B); Ogawa et al U.S. Patents 4,786,588 and 4,791,053; Hasebe et al U.S. Patents 4,820,624 and 4,865,962; Sugimoto and Miyake, "Mechanism of Halide Conversion Process of Colloidal AgCl Microcrystals by Br Ions", Parts I and II, *Journal of Colloid and Interface Science*, Vol. 140, No. 2, Dec. 1990, pp. 335-361; Houle et al U.S. Patent 5,035,992; and Japanese published applications (Kokai) 252649-A (priority 02.03.90-JP 051165 Japan) and 288143-A (priority 04.04.90-JP 089380 Japan); and published European Patent Applications 273 430, 341 728, and 531 799.

[0067] The emulsions used in this invention can be chemically sensitized with active gelatin as illustrated by T. H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, pp. 67-76, or with sulfur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, rhenium or phosphorus sensitizers or combinations of these sensitizers, (particularly combinations of sulfur with gold or selenium), such as at pAg levels of from 5 to 10, pH levels of from 5 to 8 and temperatures of from 30 to 80°C, as illustrated by *Research Disclosure*, Vol. 120, April, 1974, Item 12008, *Research Disclosure*, Vol. 134, June, 1975, Item 13452, Sheppard et al U.S. Patent 1,623,499, Matthies et al U.S. Patent 1,673,522, Waller et al U.S. Patent 2,399,083, Damschroder et al U.S. Patent 2,642,361, McVeigh U.S. Patent 3,297,447, Dunn U.S. Patent 3,297,446, McBride U.K. Patent 1,315,755, Berry et al U.S. Patent 3,772,031, Gilman et al U.S. Patent 3,761,267, Ohi et al U.S. Patent 3,857,711, Klinger et al U.S. Patent 3,565,633, Oftedahl U.S. Patents 3,901,714 and 3,904,415, Simons U.K. Patent 1,396,696 and Deaton U.S. Patent 5,049,485, chemical sensitization being optionally conducted in the presence of thiocyanate derivatives as described in Damschroder U.S. Patent 2,642,361; thioether compounds as disclosed in Lowe et al U.S. Patent 2,521,926, Williams et al U.S. Patent 3,021,215 and Bigelow U.S. Patent 4,054,457; and azaindenes, azapyridazines and azapyrimidines as described in Dostes U.S. Patent 3,411,914, Kuwabara et al U.S. Patent 3,554,757, Oguchi et al U.S. Patent 3,565,631 and Oftedahl U.S. Patent 3,901,714; elemental sulfur as described by Miyoshi et al published European Patent Application 294 149 and

Tanaka et al published European Patent Application 297 804; and thiosulfonates as described by Nishikawa et al published European Patent Application 293 917. Additionally or alternatively, the emulsions can be reduction-sensitized--e.g., with hydrogen, as illustrated by Janusonis U.S. Patent 3,891,446 and Babcock et al U.S. Patent 3,984,249, by low pAg (e.g., less than 5), high pH (e.g., greater than 8) treatment, or through the use of reducing agents such as stannous chloride, thiourea dioxide, polyamines and amineboranes as illustrated by Allen et al U.S. Patent 2,983,609, Oftedahl et al *Research Disclosure*, Vol. 136, August, 1975, Item 13654, Lowe et al U.S. Patents 2,518,698 and 2,739,060, Roberts et al U.S. Patents 2,743,182 and '183, Chambers et al U.S. Patent 3,026,203 and Bigelow et al U.S. Patent 3,361,564.

[0068] Chemical sensitization can take place in the presence of spectral sensitizing dyes as described by Philippaerts et al U.S. Patent 3,628,960, Kofron et al U.S. Patent 4,439,520, Dickerson U.S. Patent 4,520,098, Maskasky U.S. Patent 4,435,501, Ihama et al U.S. Patent 4,693,965 and Ogawa U.S. Patent 4,791,053. Chemical sensitization can be directed to specific sites or crystallographic faces on the silver halide grain as described by Haugh et al U.K. Patent Application 2,038,792A and Mifune et al published European Patent Application 302 528. The sensitivity centers resulting from chemical sensitization can be partially or totally occluded by the precipitation of additional layers of silver halide using such means as twin-jet additions or pAg cycling with alternate additions of silver and halide salts as described by Morgan U.S. Patent 3,917,485, Becker U.S. Patent 3,966,476 and *Research Disclosure*, Vol. 181, May, 1979, Item 18155. Also as described by Morgan, cited above, the chemical sensitizers can be added prior to or concurrently with the additional silver halide formation. Chemical sensitization can take place during or after halide conversion as described by Hasebe et al published European Patent Application 273 404. In many instances epitaxial deposition onto selected tabular grain sites (e.g., edges or corners) can either be used to direct chemical sensitization or to itself perform the functions normally performed by chemical sensitization.

[0069] The emulsions used in the invention can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines (i.e., tri-, tetra- and polynuclear cyanines and merocyanines), styryls, merostyryls, streptocyanines, hemicyanines, arylidenes, allopolar cyanines and enamine cyanines.

[0070] The cyanine spectral sensitizing dyes include, joined by a methine linkage, two basic heterocyclic nuclei, such as those derived from quinolinium, pyridinium, isoquinolinium, 3H-indolium, benzindolium, oxazolium, thiazolium, selenazolinium, imidazolium, benzoxazolium, benzothiazolium, benzoselenazolium, benzotellurazolium, benzimidazolium, naphthoxazolium, naphthothiazolium, naphthoselenazolium, naphtotellurazolium, thiazolinium, dihydronaphthothiazolium, pyrylium and imidazopyrazinium quaternary salts.

[0071] The merocyanine spectral sensitizing dyes include, joined by a methine linkage, a basic heterocyclic nucleus of the cyanine-dye type and an acidic nucleus such as can be 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, cyclohexan-1,3-dione, 1,3-dioxane-4,6-dione, pyrazolin-3,5-dione, pentan-2,4-dione, alkylsulfonyl acetonitrile, benzoylacetone, malononitrile, malonamide, isoquinolin-4-one, chroman-2,4-dione, 5H-furan-2-one, 5H-3-pyrrolin-2-one, 1,1,3-tricyanopropene and telluracyclohexanedione.

[0072] One or more spectral sensitizing dyes may be employed. Dyes with sensitizing maxima at wavelengths throughout the visible and infrared spectrum and with a great variety of spectral sensitivity curve shapes are known. The choice and relative proportions of dyes depends upon the region of the spectrum to which sensitivity is desired and upon the shape of the spectral sensitivity curve desired. An example of a material which is sensitive in the infrared spectrum is shown in Simpson et al., U.S. Patent 4,619,892, which describes a material which produces cyan, magenta and yellow dyes as a function of exposure in three regions of the infrared spectrum (sometimes referred to as "false" sensitization). Dyes with overlapping spectral sensitivity curves will often yield in combination a curve in which the sensitivity at each wavelength in the area of overlap is approximately equal to the sum of the sensitivities of the individual dyes. Thus, it is possible to use combinations of dyes with different maxima to achieve a spectral sensitivity curve with a maximum intermediate to the sensitizing maxima of the individual dyes.

[0073] Combinations of spectral sensitizing dyes can be used which result in supersensitization--that is, spectral sensitization greater in some spectral region than that from any concentration of one of the dyes alone or that which would result from the additive effect of the dyes. Supersensitization can be achieved with selected combinations of spectral sensitizing dyes and other addenda such as stabilizers and antifoggants, development accelerators or inhibitors, coating aids, brighteners and antistatic agents. Any one of several mechanisms, as well as compounds which can be responsible for supersensitization, are discussed by Gilman, *Photographic Science and Engineering*, Vol. 18, 1974, pp. 418-430.

[0074] Spectral sensitizing dyes can also affect the emulsions in other ways. For example, spectrally sensitizing dyes can increase photographic speed within the spectral region of inherent sensitivity. Spectral sensitizing dyes can also function as antifoggants or stabilizers, development accelerators or inhibitors, reducing or nucleating agents, and halogen acceptors or electron acceptors, as disclosed in Brooker et al U.S. Patent 2,131,038, Illingsworth et al U.S. Patent 3,501,310, Webster et al U.S. Patent 3,630,749, Spence et al U.S. Patent 3,718,470 and Shiba et al U.S. Patent

3,930,860.

[0075] Among useful spectral sensitizing dyes for sensitizing the emulsions described herein are those found in U. K. Patent 742,112, Brooker U.S. Patents 1,846,300, '301, '302, '303, '304, 2,078,233 and 2,089,729, Brooker et al U. S. Patents 2,165,338, 2,213,238, 2,493,747, '748, 2,526,632, 2,739,964 (Reissue 24,292), 2,778,823, 2,917,516, 3,352,857, 3,411,916 and 3,431,111, Sprague U.S. Patent 2,503,776, Nys et al U.S. Patent 3,282,933, Riester U.S. Patent 3,660,102, Kampfner et al U.S. Patent 3,660,103, Taber et al U.S. Patents 3,335,010, 3,352,680 and 3,384,486, Lincoln et al U.S. Patent 3,397,981, Fumia et al U.S. Patents 3,482,978 and 3,623,881, Spence et al U.S. Patent 3,718,470 and Mee U.S. Patent 4,025,349. Examples of useful supersensitizing-dye combinations, of non-light-absorbing addenda which function as supersensitizers or of useful dye combinations are found in McFall et al U.S. Patent 2,933,390, Jones et al U.S. Patent 2,937,089, Motter U.S. Patent 3,506,443 and Schwan et al U.S. Patent 3,672,898.

[0076] Spectral sensitizing dyes can be added at any stage during the emulsion preparation. They may be added at the beginning of or during precipitation as described by Wall, *Photographic Emulsions*, American Photographic Publishing Co., Boston, 1929, p. 65, Hill U.S. Patent 2,735,766, Philippaerts et al U.S. Patent 3,628,960, Locker U.S. Patent 4,183,756, Locker et al U.S. Patent 4,225,666 and *Research Disclosure*, Vol. 181, May, 1979, Item 18155, and Tani et al published European Patent Application 301 508. They can be added prior to or during chemical sensitization as described by Kofron et al U.S. Patent 4,439,520, Dickerson U.S. Patent 4,520,098, Maskasky U.S. Patent 4,435,501 and Philippaerts et al cited above. They can be added before or during emulsion washing as described by Asami et al published European Patent Application 287 100 and Metoki et al published European Patent Application 291 399. The dyes can be mixed in directly before coating as described by Collins et al U.S. Patent 2,912,343. Small amounts of iodide can be adsorbed to the emulsion grains to promote aggregation and adsorption of the spectral sensitizing dyes as described by Dickerson cited above. Postprocessing dye stain can be reduced by the proximity to the dyed emulsion layer of fine high iodide grains as described by Dickerson. Depending on their solubility, the spectral sensitizing dyes can be added to the emulsion as solutions in water or such solvents as methanol, ethanol, acetone or pyridine; dissolved in surfactant solutions as described by Sakai et al U.S. Patent 3,822,135; or as dispersions as described by Owens et al U.S. Patent 3,469,987 and Japanese published Patent Application (Kokai) 24185/71. The dyes can be selectively adsorbed to particular crystallographic faces of the emulsion grain as a means of restricting chemical sensitization centers to other faces, as described by Mifune et al published European Patent Application 302 528. The spectral sensitizing dyes may be used in conjunction with poorly adsorbed luminescent dyes, as described by Miyasaka et al published European Patent Applications 270 079, 270 082 and 278 510.

[0077] The following illustrate specific spectral sensitizing dye selections:

SS-1

Anhydro-5'-chloro-3'-di-(3-sulfopropyl)naphtho[1,2-d]thiazolothiocyanine hydroxide, sodium salt

SS-2

Anhydro-5'-chloro-3'-di-(3-sulfopropyl)naphtho[1,2-d]oxazolothiocyanine hydroxide, sodium salt

SS-3

Anhydro-4,5-benzo-3'-methyl-4'-phenyl-1-(3-sulfopropyl)naphtho[1,2-d]thiazolothiazolocyanine hydroxide

SS-4

1,1'-Diethylnaphtho[1,2-d]thiazolo-2'-cyanine bromide

SS-5

Anhydro-1,1'-dimethyl-5,5'-di-(trifluoromethyl)-3-(4-sulfobutyl)-3'-(2,2,2-trifluoroethyl)benzimidazolocarbo-
cyanine hydroxide

SS-6

Anhydro-3,3'-(2-methoxyethyl)-5,5'-diphenyl-9-ethylloxacarbo-cyanine, sodium salt

SS-7

Anhydro-11-ethyl-1,1'-di-(3-sulfopropyl)naphtho[1,2-d]oxazolocarbo-cyanine hydroxide, sodium salt

SS-8

Anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)-oxaselenacarbo-cyanine hydroxide, sodium salt

SS-9

5,6-Dichloro-3',3'-dimethyl-1,1',3-triethylbenzimidazolo-3H-indolocarbo-cyanine bromide

SS-10

Anhydro-5,6-dichloro-1,1-diethyl-3-(3-sulfopropyl)benzimidazolooxacarbo-cyanine hydroxide

SS-11

Anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(2-sulfoethylcarbamoylmethyl)thiacarbo-cyanine hydroxide, sodium salt

SS-12

Anhydro-5',6'-dimethoxy-9-ethyl-5-phenyl-3-(3-sulfobutyl)-3'-(3-sulfopropyl)oxathiacarbo-cyanine hydroxide,
sodium salt

SS-13

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- Anhydro-5,5'-dichloro-9-ethyl-3-(3-phosphonopropyl)-3'-(3-sulfopropyl)thiacarbocyanine hydroxide
 SS-14
- Anhydro-3,3'-di-(2-carboxyethyl)-5,5'-dichloro-9-ethyl-thiacarbocyanine bromide
 SS-15
- 5 Anhydro-5,5'-dichloro-3-(2-carboxyethyl)-3'-(3-sulfopropyl)thiacyanine sodium salt
 SS-16
- 9-(5-Barbituric acid)-3,5-dimethyl-3'-ethyltellurathiacarbocyanine bromide
 SS-17
- 10 Anhydro-5,6-methylenedioxy-9-ethyl-3-methyl-3'-(3-sulfopropyl)tellurathiacarbocyanine hydroxide
 SS-18
- 3-Ethyl-6,6'-dimethyl-3'-pentyl-9,11-neopentylenethiadicarbocyanine bromide
 SS-19
- Anhydro-3-ethyl-9,11-neopentylene-3'-(3-sulfopropyl)-thiadicarbocyanine hydroxide
 SS-20
- 15 Anhydro-3-ethyl-11,13-neopentylene-3'-(3-sulfopropyl)-oxathiatricarbocyanine hydroxide, sodium salt
 SS-21
- Anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt
 SS-22
- 20 Anhydro-5,5'-diphenyl-3,3'-di-(3-sulfobutyl)-9-ethyloxacarbocyanine hydroxide, sodium salt
 SS-23
- Anhydro-5,5'-dichloro-3,3'-di-(3-sulfopropyl)-9-ethylthiacarbocyanine hydroxide, triethylammonium salt
 SS-24
- Anhydro-5,5'-dimethyl-3,3'-di-(3-sulfopropyl)-9-ethylthiacarbocyanine hydroxide, sodium salt
 SS-25
- 25 Anhydro-5,6-dichloro-1-ethyl-3-(3-sulfobutyl)-1'-(3-sulfopropyl)benzimidazonaphtho[1,2-d]thiazolocarbo-
 anine hydroxide, triethylammonium salt
 SS-26
- Anhydro-11-ethyl-1,1'-di-(3-sulfopropyl)naphth[1,2-d]-oxazolocarbo-
 anine hydroxide, sodium salt
 SS-27
- 30 Anhydro-3,9-diethyl-3'-methylsulfonylcarbamoylemethyl-5-phenyloxathiacarbocyanine *p*-toluenesulfonate
 SS-28
- Anhydro-6,6'-dichloro-1,1'-diethyl-3,3'-di-(3-sulfopropyl)-5,5'-bis(trifluoromethyl)benzimidazolocarbo-
 cyanine hydroxide, sodium salt
 SS-29
- 35 Anhydro-5'-chloro-5-phenyl-3,3'-di-(3-sulfopropyl)-oxathiacyanine hydroxide, sodium salt
 SS-30
- Anhydro-5,5'-dichloro-3,3'-di-(3-sulfopropyl)thiacyanine hydroxide, sodium salt
 SS-31
- 40 3-Ethyl-5-[1,4-dihydro-1-(4-sulfobutyl)pyridin-4-ylidene]rhodanine, triethylammonium salt
 SS-32
- 1-Carboxyethyl-5-[2-(3-ethylbenzoxazolin-2-ylidene)-ethylidene]-3-phenylthiohydantoin
 SS-33
- 45 4-[2-((1,4-Dihydro-1-dodecylpyridin-ylidene)ethylidene)-3-phenyl-2-isoxazolin-5-one
 SS-34
- 5-(3-Ethylbenzoxazolin-2-ylidene)-3-phenylrhodanine
 SS-35
- 1,3-Diethyl-5-[[1-ethyl-3-(3-sulfopropyl)benzimidazolin-2-ylidene]ethylidene]-2-thiobarbituric acid
 SS-36
- 50 5-[2-(3-Ethylbenzoxazolin-2-ylidene)ethylidene]-1-methyl-2-dimethylamino-4-oxo-3-phenylimidazolium *p*-
 toluenesulfonate
 SS-37
- 5-[2-(5-Carboxy-3-methylbenzoxazolin-2-ylidene)ethylidene]-3-cyano-4-phenyl-1-(4-methylsulfonamido)-
 3-pyrrolin-5-one
 SS-38
- 55 2-[4-(Hexylsulfonamido)benzoylcyanomethine]-2-[2-{3-(2-methoxyethyl)-5-[(2-methoxyethyl)sulfonamido]-
 benzoxazolin-2-ylidene}ethylidene]acetonitrile
 SS-39

3-Methyl-4-[2-(3-ethyl-5,6-dimethylbenzotellurazolin-2-ylidene)ethylidene]-1-phenyl-2-pyrazolin-5-one
SS-40

3-Heptyl-1-phenyl-5-[4-[3-(3-sulfobutyl)-naphtho[1,2-d]thiazolin]-2-butenylidene]-2-thiohydantoin
SS-41

1,4-Phenylene-bis(2-aminovinyl-3-methyl-2-thiazolinium] dichloride
SS-42

Anhydro-4-{2-[3-(3-sulfopropyl)thiazolin-2-ylidene]-ethylidene}-2-{3-[3-(3-sulfopropyl)thiazolin-2-ylidene]propenyl-5-oxazolium, hydroxide, sodium salt
SS-43

3-Carboxymethyl-5-{3-carboxymethyl-4-oxo-5-methyl-1,3,4-thiadiazolin-2-ylidene)ethylidene]thiazolin-2-ylidene}rhodanine, dipotassium salt
SS-44

1,3-Diethyl-5-[1-methyl-2-(3,5-dimethylbenzotellurazolin-2-ylidene)ethylidene]-2-thiobarbituric acid
SS-45

3-Methyl-4-[2-(3-ethyl-5,6-dimethylbenzotellurazolin-2-ylidene)-1-methylethylidene]-1-phenyl-2-pyrazolin-5-one
SS-46

1,3-Diethyl-5-[1-ethyl-2-(3-ethyl-5,6-dimethoxybenzotellurazolin-2-ylidene)ethylidene]-2-thiobarbituric acid
SS-47

3-Ethyl-5-[(ethylbenzothiazolin-2-ylidene)-methyl]-[(1,5-dimethylnaphtho[1,2-d]selenazolin-2-ylidene)methyl]methylene}rhodanine
SS-48

5-[Bis[(3-ethyl-5,6-dimethylbenzothiazolin-2-ylidene)-methyl]methylene]-1,3-diethyl-barbituric acid
SS-49

3-Ethyl-5-[(3-ethyl-5-methylbenzotellurazolin-2-ylidene)methyl][1-ethylnaphtho[1,2-d]-tellurazolin-2-ylidene)methyl]methylene}rhodanine
SS-50

Anhydro-5,5'-diphenyl-3,3'-di-(3-sulfopropyl)thiacyanine hydroxide, triethylammonium salt
SS-51

Anhydro-5-chloro-5'-phenyl-3,3'-di-(3-sulfopropyl) thiacyanine hydroxide, triethylammonium salt

[0078] Additional suitable spectral sensitizing dyes are included in the Examples.

[0079] Instability which increases minimum density in negative-type emulsion coatings (i.e., fog) can be protected against by incorporation of stabilizers, antifoggants, antikinking agents, latent-image stabilizers and similar addenda in the emulsion and contiguous layers prior to coating. Most of the antifoggants effective in the emulsions used in this invention can also be used in developers and can be classified under a few general headings, as illustrated by C.E.K. Mees, *The Theory of the Photographic Process*, 2nd Ed., Macmillan, 1954, pp. 677-680.

[0080] To avoid such instability in emulsion coatings, stabilizers and antifoggants can be employed, such as halide ions (e.g., bromide salts); chloropalladates and chloropalladites as illustrated by Trivelli et al U.S. Patent 2,566,263; water-soluble inorganic salts of magnesium, calcium, cadmium, cobalt, manganese and zinc as illustrated by Jones U.S. Patent 2,839,405 and Sidebotham U.S. Patent 3,488,709; mercury salts as illustrated by Allen et al U.S. Patent 2,728,663; selenols and diselenides as illustrated by Brown et al U.K. Patent 1,336,570 and Pollet et al U.K. Patent 1,282,303; quaternary ammonium salts of the type illustrated by Allen et al U.S. Patent 2,694,716, Brooker et al U.S. Patent 2,131,038, Graham U.S. Patent 3,342,596 and Arai et al U.S. Patent 3,954,478; azomethine desensitizing dyes as illustrated by Thiers et al U.S. Patent 3,630,744; isothioureas derivatives as illustrated by Herz et al U.S. Patent 3,220,839 and Knott et al U.S. Patent 2,514,650; thiazolidines as illustrated by Scavron U.S. Patent 3,565,625; peptide derivatives as illustrated by Maffet U.S. Patent 3,274,002; pyrimidines and 3-pyrazolidones as illustrated by Welsh U.S. Patent 3,161,515 and Hood et al U.S. Patent 2,751,297; azotriazoles and azotetrazoles as illustrated by Baldassarri et al U.S. Patent 3,925,086; azaindenes, particularly tetraazaindenes, as illustrated by Heimbach U.S. Patent 2,444,605, Knott U.S. Patent 2,933,388, Williams U.S. Patent 3,202,512, *Research Disclosure*, Vol. 134, June, 1975, Item 13452, and Vol. 148, August, 1976, Item 14851, and Nepker et al U.K. Patent 1,338,567; mercaptotetrazoles, -triazoles and -diazoles as illustrated by Kendall et al U.S. Patent 2,403,927, Kennard et al U.S. Patent 3,266,897, *Research Disclosure*, Vol. 116, December, 1973, Item 11684, Luckey et al U.S. Patent 3,397,987 and Salesin U.S. Patent 3,708,303; azoles as illustrated by Peterson et al U.S. Patent 2,271,229 and *Research Disclosure*, Item 11684, cited above; purines as illustrated by Sheppard et al U.S. Patent 2,319,090, Birr et al U.S. Patent 2,152,460, *Research Disclosure*, Item 13452, cited above, and Dostes et al French Patent 2,296,204, polymers of 1,3-dihydroxy(and/or 1,3-carbamoxy)-2-methylenepropane as illustrated by Saleck et al U.S. Patent 3,926,635 and tellurazoles, tellurazolines, tellurazolinium salts and tellurazolium salts as illustrated by Gunther et al U.S. Patent 4,661,438, aromatic ox-

atellurazinium salts as illustrated by Gunther, U.S. Patent 4,581,330 and Przyklek-Elling et al U.S. Patents 4,661,438 and 4,677,202. High chloride emulsions can be stabilized by the presence, especially during chemical sensitization, of elemental sulfur as described by Miyoshi et al European published Patent Application 294 149 and Tanaka et al published European Patent Application 297 804 and thiosulfonates as described by Nishikawa et al published European Patent Application 293 917.

[0081] Among useful stabilizers for gold sensitized emulsions are water-insoluble gold compounds of benzothiazole, benzoxazole, naphthothiazole and certain merocyanine and cyanine dyes, as illustrated by Yutzy et al U.S. Patent 2,597,915, and sulfinamides, as illustrated by Nishio et al U.S. Patent 3,498,792.

[0082] Among useful stabilizers in layers containing poly(alkylene oxides) are tetraazaindenes, particularly in combination with Group VIII noble metals or resorcinol derivatives, as illustrated by Carroll et al U.S. Patent 2,716,062, U. K. Patent 1,466,024 and Habu et al U.S. Patent 3,929,486; quaternary ammonium salts of the type illustrated by Piper U.S. Patent 2,886,437; water-insoluble hydroxides as illustrated by Maffet U.S. Patent 2,953,455; phenols as illustrated by Smith U.S. Patents 2,955,037 and '038; ethylene diurea as illustrated by Dersch U.S. Patent 3,582,346; barbituric acid derivatives as illustrated by Wood U.S. Patent 3,617,290; boranes as illustrated by Bigelow U.S. Patent 3,725,078; 3-pyrazolidinones as illustrated by Wood U.K. Patent 1,158,059 and aldoximes, amides, anilides and esters as illustrated by Butler et al U.K. Patent 988,052.

[0083] The high chloride {100} tabular grain emulsions described herein can be protected from fog and desensitization caused by trace amounts of metals such as copper, lead, tin, iron and the like by incorporating addenda such as sulfocatechol-type compounds, as illustrated by Kennard et al U.S. Patent 3,236,652; aldoximes as illustrated by Carroll et al U.K. Patent 623,448 and *meta*- and polyphosphates as illustrated by Draisbach U.S. Patent 2,239,284, and carboxylic acids such as ethylenediamine tetraacetic acid as illustrated by U.K. Patent 691,715.

[0084] Among stabilizers useful in layers containing synthetic polymers of the type employed as vehicles and to improve covering power are monohydric and polyhydric phenols as illustrated by Forsgard U.S. Patent 3,043,697; saccharides as illustrated by U.K. Patent 897,497 and Stevens et al U.K. Patent 1,039,471, and quinoline derivatives as illustrated by Dersch et al U.S. Patent 3,446,618.

[0085] Among stabilizers useful in protecting the emulsion layers against dichroic fog are addenda such as salts of nitron as illustrated by Barbier et al U.S. Patents 3,679,424 and 3,820,998; mercaptocarboxylic acids as illustrated by Willems et al U.S. Patent 3,600,178; and addenda listed by E. J. Birr, *Stabilization of Photographic Silver Halide Emulsions*, Focal Press, London, 1974, pp. 126-218.

[0086] Among stabilizers useful in protecting emulsion layers against development fog are addenda such as azabenzimidazoles as illustrated by Bloom et al U.K. Patent 1,356,142 and U.S. Patent 3,575,699, Rogers U.S. Patent 3,473,924 and Carlson et al U.S. Patent 3,649,267; substituted benzimidazoles, benzothiazoles, benzotriazoles and the like as illustrated by Brooker et al U.S. Patent 2,131,038, Land U.S. Patent 2,704,721, Rogers et al U.S. Patent 3,265,498; mercapto-substituted compounds, e.g., mercaptotetrazoles, as illustrated by Dimsdale et al U.S. Patent 2,432,864, Rauch et al U.S. Patent 3,081,170, Weyerts et al U.S. Patent 3,260,597, Grasshoff et al U.S. Patent 3,674,478 and Arond U.S. Patent 3,706,557; isothiourea derivatives as illustrated by Herz et al U.S. Patent 3,220,839, and thiodiazole derivatives as illustrated by von Konig U.S. Patent 3,364,028 and von Konig et al U.K. Patent 1,186,441.

[0087] Where hardeners of the aldehyde type are employed, the emulsion layers can be protected with antifoggants such as monohydric and polyhydric phenols of the type illustrated by Sheppard et al U.S. Patent 2,165,421; nitro-substituted compounds of the type disclosed by Rees et al U.K. Patent 1,269,268; poly(alkylene oxides) as illustrated by Valbusa U.K. Patent 1,151,914, and mucohalogenic acids in combination with urazoles as illustrated by Allen et al U.S. Patents 3,232,761 and 3,232,764, or further in combination with maleic acid hydrazide as illustrated by Rees et al U.S. Patent 3,295,980.

[0088] To protect emulsion layers coated on linear polyester supports, addenda can be employed such as parabanic acid, hydantoin acid hydrazides and urazoles as illustrated by Anderson et al U.S. Patent 3,287,135, and piazines containing two symmetrically fused 6-member carbocyclic rings, especially in combination with an aldehyde-type hardening agent, as illustrated in Rees et al U.S. Patent 3,396,023.

[0089] Kink desensitization of the emulsions can be reduced by the incorporation of thallos nitrate as illustrated by Overman U.S. Patent 2,628,167; compounds, polymeric lattices and dispersions of the type disclosed by Jones et al U.S. Patents 2,759,821 and '822;azole and mercaptotetrazole hydrophilic colloid dispersions of the type disclosed by *Research Disclosure*, Vol. 116, December, 1973, Item 11684; plasticized gelatin compositions of the type disclosed by Milton et al U.S. Patent 3,033,680; water-soluble interpolymers of the type disclosed by Rees et al U.S. Patent 3,536,491; polymeric lattices prepared by emulsion polymerization in the presence of poly(alkylene oxide) as disclosed by Pearson et al U.S. Patent 3,772,032, and gelatin graft copolymers of the type disclosed by Rakoczy U.S. Patent 3,837,861.

[0090] Where the color photographic elements are intended to be processed at elevated bath or drying temperatures, as in rapid access processors, pressure desensitization and/or increased fog can be controlled by selected combinations of addenda, vehicles, hardeners and/or processing conditions as illustrated by Abbott et al U.S. Patent 3,295,976,

Barnes et al U.S. Patent 3,545,971, Salesin U.S. Patent 3,708,303, Yamamoto et al U.S. Patent 3,615,619, Brown et al U.S. Patent 3,623,873, Taber U.S. Patent 3,671,258, Abele U.S. Patent 3,791,830, *Research Disclosure*, Vol. 99, July, 1972, Item 9930, Florens et al U.S. Patent 3,843,364, Priem et al U.S. Patent 3,867,152, Adachi et al U.S. Patent 3,967,965 and Mikawa et al U.S. Patents 3,947,274 and 3,954,474.

5 **[0091]** In addition to increasing the pH or decreasing the pAg of an emulsion and adding gelatin, which are known to retard latent-image fading, latent-image stabilizers can be incorporated, such as amino acids, as illustrated by Ezekiel U.K. Patents 1,335,923, 1,378,354, 1,387,654 and 1,391,672, Ezekiel et al U.K. Patent 1,394,371, Jefferson U.S. Patent 3,843,372, Jefferson et al U.K. Patent 1,412,294 and Thurston U.K. Patent 1,343,904; carbonyl-bisulfite addition products in combination with hydroxybenzene or aromatic amine developing agents as illustrated by Seiter et al U.S. Patent 3,424,583; cycloalkyl-1,3-diones as illustrated by Beckett et al U.S. Patent 3,447,926; enzymes of the catalase type as illustrated by Matejec et al U.S. Patent 3,600,182; halogen-substituted hardeners in combination with certain cyanine dyes as illustrated by Kumai et al U.S. Patent 3,881,933; hydrazides as illustrated by Honig et al U.S. Patent 3,386,831; alkenyl benzothiazolium salts as illustrated by Arai et al U.S. Patent 3,954,478; hydroxy-substituted benzylidene derivatives as illustrated by Thurston U.K. Patent 1,308,777 and Ezekiel et al U.K. Patents 1,347,544 and 1,353,527; mercapto-substituted compounds of the type disclosed by Sutherns U.S. Patent 3,519,427; metal-organic complexes of the type disclosed by Matejec et al U.S. Patent 3,639,128; penicillin derivatives as illustrated by Ezekiel U.K. Patent 1,389,089; propynylthio derivatives of benzimidazoles, pyrimidines, etc., as illustrated by von Konig et al U.S. Patent 3,910,791; combinations of iridium and rhodium compounds as disclosed by Yamasue et al U.S. Patent 3,901,713; sydnones or sydnone imines as illustrated by Noda et al U.S. Patent 3,881,939; thiazolidine derivatives as illustrated by Ezekiel U.K. Patent 1,458,197 and thioether-substituted imidazoles as illustrated by *Research Disclosure*, Vol. 136, August, 1975, Item 13651.

10 **[0092]** The dye image providing compounds incorporated in the color photographic elements of this invention can take any convenient conventional form. A general description of dye image providing compounds useful in color photographic elements is provided in *Research Disclosure*, Item 308119, cited above, Section VII. The dye image providing compound is typically a dye image forming coupler (hereinafter referred to as a coupler), although other dye image providing compounds, such as a dye redox releaser compound, a dye developer compound, an oxichromic developer compound, or a bleachable dye or dye precursor compound are also contemplated. Dye redox releaser, dye developer, and oxichromic developer compounds useful in color photographic elements are described in *The Theory of the Photographic Process*, 4th edition, T.H. James, editor, Macmillan, New York, 1977, Chapter 12, Section V, and in Section XXIII of *Research Disclosure*, Item 308119, cited above. Dye compounds useful in color photographic elements employed in dye bleach processes are described in Chapter 12, Section IV, of *The Theory of the Photographic Process*, 4th edition.

15 **[0093]** A coupler compound contains a coupler moiety COUP, which is combined with oxidized developing agent a coupling reaction to form an image dye. A coupler compound can additionally contain a group, called a coupling-off group, that is attached to the coupler moiety by a bond that is cleaved upon reaction of the coupler compound with oxidized color developing agent. Coupling-off groups can be halogen, such as chloro, bromo, fluoro, and iodo, or organic radicals that are attached to the coupler moieties by atoms such as oxygen, sulfur, nitrogen, and phosphorus.

20 **[0094]** Following is a listing of patents and publications that describe representative coupler compounds that contain COUP groups useful in the invention:

25 **[0095]** Couplers which form cyan dyes upon reaction with oxidized color developing agents are described in such representative patents and publications as: U.S. Patent Nos. 2,772,162; 2,895,826; 3,002,836; 3,034,892; 2,474,293; 2,423,730; 2,367,531; 3,041,236; 4,333,999, "Farbkuppler-eine Literaturubersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961), and Section VII D of *Research Disclosure*, Item 308119, cited above. Preferably such couplers are phenols and naphthols.

30 **[0096]** Couplers which form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,600,788; 2,369,489; 2,343,703; 2,311,082; 3,152,896; 3,519,429; 3,062,653; 2,908,573, "Farbkuppler-eine Literaturubersicht," published in Agfa Mitteilungen, Band III, pp. 126-156 (1961), and Section VII D of *Research Disclosure*, Item 308119, cited above. Preferably such couplers are pyrazolones or pyrazolotriazoles.

35 **[0097]** Couplers which form yellow dyes upon reaction with oxidized and color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,875,057; 2,407,210; 3,265,506; 2,298,443; 3,048,194; 3,447,928, "Farbkuppler-eine Literaturubersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961), and Section VII D of *Research Disclosure*, Item 308119, cited above. Preferably such couplers are acylacetamides, such as benzoylacetamides and pivaloylacetamides.

40 **[0098]** In a preferred form the color photographic elements of the invention are employed to form color prints for viewing. When the color photographic elements of the invention are intended to be used as taking films (i.e., to form a image that is subsequently printed employing a separate element), in addition to the dye image forming couplers, it is preferred to incorporate masking couplers, such disclosed by *Research Disclosure*, Item 308119, cited above, Section

VII, sub-section G, and couplers that improve image quality by releasing photographically useful groups, such development restrainers, such as disclosed in Section VII, sub-section F.

[0099] If desired, the color photographic elements can contain an applied magnetic layer, such as described in *Research Disclosure*, Vol. 343, Item Nov. 1992, Item 34390.

5 [0100] The color photographic elements can be imagewise exposed by any conventional technique employed. Contemplated exposures include those set out in *Research Disclosure*, Item 308119, cited above, Section XVIII.

[0101] Apart from the presence of high chloride {100} tabular grain emulsions the color photographic elements and their processing following imagewise exposure can take any convenient conventional form known to be useful in redox amplification dye imaging. Color photographic elements particularly intended for redox amplification dye imaging and redox amplification dye imaging processes are disclosed by Bissonette U.S. Patents 3,748,138, 3,826,652, 3,847,619, 3,856,524, 3,862,842, 3,923,511, 3,989,526, 4,002,477, 4,088,486, 4,089,685, 4,097,278 and 4,146,395; Travis U.S. Patent 3,765,891; Matejec U.S. Patents 3,674,490 and 3,776,730; Dunn et al U.S. Patent 3,822,129; Mowrey U.S. Patents 3,904,413 and 4,035,187; Barr et al U.S. Patent 4,022,616; *Research Disclosure*, Vol. 116, December 1973, Item 11660; *Research Disclosure*, Vol. 148, August 1976, Items 14836, 14846 and 14847. Note that Bissonette U.S. Patent 4,089,685 discloses a preferred reversal process.

[0102] In redox amplification dye imaging an oxidizing agent and a reducing agent are employed that are reactively inert in the absence of silver, but are catalyzed by developed silver to enter into a oxidation-reduction action. The oxidized reducing agent produced by the oxidation-reduction reaction then reacts with the dye image providing compound to form a dye image.

20 [0103] Most typically the reducing agent is a color developing agent (e.g., a *p*-phenylene-diamine). Typical preferred color developing agents include 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N-ethyl-N-(methanesulfonamido)ethylaniline sulfate hydrate, 4-amino-3-methyl-N-ethyl-N-hydroxyethylaniline sulfate, 4-amino-3-(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride, and 4-amino-N-ethyl-N-(2-methoxyethyl)-*m*-toluidine di-*p*-toluenesulfonic acid. The oxidized color developing agent produced by the oxidation-reduction reaction then reacts with the dye image providing compound, usually a coupler, to form the dye image. When the dye image providing compound is a redox dye releaser, the reducing agent is an electron transfer agent (e.g., an aminophenol, 3-pyrazolidinone, a *p*-phenylenediamine or a reductone). Typical preferred redox dye releasers and electron transfer agents are set out in *Research Disclosure*, Vol. 151, Nov. 1976, Item 15162.

[0104] Useful oxidizing agents can be selected from among transition metal ion complexes (e.g., cobalt(III) and ruthenium(III) complexes containing ammine and/or amine ligands). Cobalt hexammine is a specifically preferred transition metal ion complex useful as an oxidizing agent. Peroxy compounds (e.g., hydrogen peroxide and compounds that provide hydrogen peroxide, such as alkali metal perborates, percarbonates and periodates) are also useful as oxidizing agents. Hydrogen peroxide is a specifically preferred oxidizing agent. Mixtures of oxidizing agents can be employed, if desired.

35 [0105] Development in a first processing solution of an imagewise exposed color photographic element according to the invention, followed by redox amplification dye imaging is a second processing solution, following by undeveloped grain removal by fixing in a third processing solution and removal of developed silver by bleaching in a fourth processing solution can be undertaken. Combined bleaching and fixing baths, referred to as blixing baths, are well known in the art and are specifically contemplated. One of the outstanding advantages of the present invention is that the low silver coverages in the color photographic elements allows the silver bleaching step to be omitted. This eliminates the conventional processing step that is generally regarded as the most objectionable, both in terms of actual performance and in terms of the environmental burden of the reaction products produced. Since the silver coating coverages are low and retained silver is tolerable, the fixing step can also be omitted. However, because this step is generally not burdensome, it is preferred to include fixing within the overall process. Since the reducing agents employed in the redox amplification dye imaging step are themselves silver halide developing agents in many instances, it is recognized that the development and redox amplification dye imaging can take place in the same processing solution, thereby simplifying the process. It is, in fact, possible to conduct the processing entirely within a single bath, referred to as a monobath. The patents cited above to illustrate redox amplification processing provide specific examples of monobaths and their use. The relatively high solubility and development rates of high chloride emulsions as well as the higher environmental tolerance of chloride ion than bromide or iodide ion, offer additional important advantages to the practice of the invention.

Examples

55 [0106] The invention can be better appreciated by reference to the following specific examples.

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Emulsion 1 High-Aspect-Ratio High-Chloride {100} Tabular Grain Emulsion

Emulsion 1A

5 [0107] A stirred reaction vessel containing 400 mL of a solution which was 0.5% in bone gelatin, 6mM in 3-amino-1H-1,2,4-triazole, 0.040 M in NaCl, and 0.20 M in sodium acetate was adjusted to pH 6.1 at 55°C. To this solution at 55°C were added simultaneously 5.0 mL of 4 M AgNO₃ and 5.0 mL of 4 M NaCl at a rate of 5 mL/min each. The temperature of the mixture was then increased to 75°C at a constant rate requiring 12 min and then held at this temperature for 5 min. The pH was adjusted to 6.2 and held to within ±0.1 of this value, and the flow of the AgNO₃ solution
10 was resumed at 5 mL/min until 0.8 mole of Ag had been added. The flow of the NaCl solution was also resumed at a rate needed to maintain a constant pAg of 6.64.

[0108] The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 65% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.95 μm and a mean thickness of 0.165 μm. The average aspect ratio of the emulsion tabular grains was 11.8.
15

Emulsion 1B

[0109] This emulsion was prepared similar to Emulsion 1A, except that the precipitation was stopped when 0.4 mole of Ag had been added.

20 [0110] The resulting emulsion consisted of tabular grain having {100} major faces which made up 65% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.28 μm and a mean thickness of 0.130 μm. The average aspect ratio of the emulsion tabular grains was 9.8.

Emulsion 2 pH = 6.1 Nucleation, pH ≅ 3.6 Growth

25 [0111] This emulsion was prepared similar to Emulsion 1B, except that the pH of the reaction vessel was adjusted to 3.6 for the last 95% of the AgNO₃ addition.

[0112] The resulting emulsion consisted of {100} tabular grains making up 60% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.39 μm, and a mean thickness of 0.180 μm. The average aspect ratio of the emulsion tabular grains was 7.7.
30

Emulsion 3 High-Aspect-Ratio AgBrCl (10% Br) {100} Tabular-Grain Emulsion

35 [0113] This emulsion was prepared similar to Emulsion 1B, except that the salt solution was 3.6 M in NaCl and 0.4 M in NaBr.

[0114] The resulting AgBrCl (10% Br) emulsion consisted of {100} tabular grain making up 52% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.28 μm, and a mean thickness of 0.115. The average aspect ratio of the emulsion tabular grains was 11.1.

Emulsion 4 3,5-Diamino-1,2,4-Triazole as {100} Tabular Grain Nucleating Agent

[0115] This emulsion was prepared similar to Emulsion 1A, except that 3,5-diamino-1,2,4-triazole (2.4 mmole) was used as the {100} tabular grain nucleating agent.

45 [0116] The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 45% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.54 μm and a mean thickness of 0.20 μm. The average aspect ratio of the emulsion tabular grains was 7.7.

Emulsion 5 Imidazole as {100} Tabular Grain Nucleating Agent

50 [0117] This emulsion was prepared similar to Emulsion 1A, except that imidazole (9.6 mmole) was used as the {100} tabular grain nucleating agent.

[0118] The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 40% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 2.20 μm and a mean thickness of 0.23 μm. The average aspect ratio of the tabular grain emulsion was 9.6.
55

Emulsion 6 AgCl{100} Tabular Grain Emulsion Made Without Aromatic Amine Restraining Agent

[0119] To a stirred reaction vessel containing 400 mL of a solution which was 0.25 wt.% in bone gelatin low in me-

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thionine content (<4 μmoles per gram gelatin), 0.008 M in NaCl, and at pH 6.2 and 85°C were added simultaneously a 4 M AgNO_3 solution at 5.0 ml/min and a 4 M NaCl solution at a rate needed to maintain a constant pCl of 2.09. When 0.20 mole of AgNO_3 had been added, the additions were stopped for 20 sec. during which time 15 mls of a 13.3% low methionine gelatin solution was added and the pH adjusted to 6.2. The additions were resumed until a total of 0.4 mole of AgNO_3 had been added. The pH was held constant at 6.2 ± 0.1 during the precipitation.

[0120] The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 40% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 2.18 μm and a mean thickness of 0.199 μm . The average aspect ratio of the tabular grain emulsion was 11.0.

Emulsion 7 High-Aspect-Ratio High-Chloride {100} Tabular Grain Emulsion

[0121] A reaction vessel contained 2 L of a solution that was 3.5% in low methionine (oxidized) gelatin, 5.6 mM in NaCl and 0.15 mM in KI. To this stirred solution at 40°C was added simultaneously and at 60 mL/min each, 30 mL of a solution 2 M in AgNO_3 and 30 mL of a solution 1.99 M in NaCl and 0.01 M in KI. The mixture was stirred for 10 min and then 1.88 L of a solution 0.5 M in AgNO_3 was added first at 8.0 mL/min for 40 min, then the flow rate was accelerated 2X requiring 130 min. A solution 0.5 M in NaCl was concurrently added as needed to maintain a constant pCl of 2.32. To the resulting emulsion was added 20 g of phthalated gelatin and it was washed by the coagulation method of U.S. Patent No. 2,614,929, and finally resuspended in 500 mL of a 1% gelatin solution, then adjusted to a pCl of 2.07. The total gelatin content was approximately 20 g/Ag mole.

[0122] The emulsion consisted of a {100} tabular grain population making up 75% of the projected area of the emulsion grains. This population had a mean diameter of 1.66 μm , and a mean thickness of 0.11 μm .

Control Emulsion 8

[0123] A control emulsion was prepared which was an AgBr tabular grain emulsion consisting of grains having a mean diameter of 1.7 μm and a mean thickness of 0.085 μm .

Control Emulsion 9

[0124] This emulsion was a silver chloride emulsion containing cubic grains having an average grain edge length of 0.6 μm .

Control Emulsion 10

[0125] This emulsion was a silver chloride emulsion containing cubic grains having an average grain edge length of 0.75 μm .

Emulsion 11

[0126] A 2030 mL solution containing 3.52% by weight low methionine gelatin, 0.0056 M sodium chloride, and 3.35×10^{-4} potassium iodide was provided in a stirred reaction vessel. The iodide was incorporated to facilitate tabular grain nucleation, but was maintained well below that required to significantly increase blue absorption. The contents of the reaction vessel were maintained at 40°C and the pCl was 2.25.

[0127] While this solution was vigorously stirred, 40.6 mL of 2.0 M silver nitrate solution and 40.6 mL of 2.0 M sodium chloride solution were added simultaneously at a rate of 81.2 mL/min each.

[0128] The mixture was then held four minutes with the temperature remaining at 40°C. Following the hold, a 0.5 M silver nitrate solution and a 0.5 M sodium chloride solution were then added simultaneously at 10.83 mL/min for 40 minutes with the pCl maintained at 2.25. The 0.5 M silver nitrate and the 0.5 M sodium chloride solutions were then added simultaneously with a ramped linearly increasing flow from 10.83 mL/min to 16.73 mL/min over 70 minutes with the pCl maintained at 2.25. Following this, a 0.75 M silver nitrate solution and a 0.75 M sodium chloride solution were added simultaneously at 16.73 mL/min over 90 minutes with the pCl maintained at 2.25.

[0129] The resulting emulsion was a tabular grain emulsion having {100} major faces with an average ECD of 1.524 μm and an average thickness of 0.148 μm .

Example 1

[0130] A stirred 50 g portion (0.05 mole) of Emulsion 7 at 25°C was adjusted to pH 5.3 with H_2SO_4 and pCl of 2.06 with NaCl. To this emulsion was added 5 ml of a solution of 0.2 M NaBr at 0.5 mL/min. Then a solution containing 0.7

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mmole/Ag mole of the green spectral sensitizing dye, anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfo-propyl)oxacarbocyanine hydroxide, triethyl amine salt, Dye A, was added. The temperature was increased to 40°C and 4 x 10⁻⁶ mole/Ag mole of sodium thiosulfate and 2.6 x 10⁻⁶/Ag mole of potassium tetrachloroaurate were added. The mixture was heated for 15 min at 60°C. A portion of this emulsion was mixed with cyan color coupler dispersion, gelatin, surfactant, and, hardener, and made 5 x 10⁻³ M in NaCl. It was coated at 0.011 g Ag/m², 1.1 g coupler/m² and 2.2 g gelatin/m² onto paper support to make Example Coating 1.

[0131] To Control Emulsion 8 was added 0.7 mmole Dye A/Ag mole and then 20 x 10⁻⁶ mole/Ag mole of sodium thiosulfate and 13 x 10⁻⁶ mole/Ag mole of potassium tetrachloroaurate were added. The mixture was heated for 15 min at 60°C. A portion of this emulsion was mixed with cyan color coupler dispersion, gelatin, surfactant, and hardener, and made 5 x 10⁻³ M in NaCl. It was coated at 0.011 g Ag/m², 1.1 g coupler/m² and 2.2 g gelatin/m² onto paper support to make Control Coating 2.

Exposure and Processing

[0132] Example Coating 1 and Control Coating 2 were exposed for 0.1 sec to a 600 W, 3,000 K tungsten light source through a 0-4.0 density step-tablet. The exposed coatings were developed for 10 sec. at 20°C in a developer having the following composition: 10 g 4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine p-toluenesulfonate, 20 g potassium carbonate, 4 g potassium sulfite, distilled water to 2 L and just before use 20 mL of 30 % hydrogen peroxide was added. The coatings were then put into a 1% acetic acid stop bath and then water washed. No bleach or fix baths were needed. The results are given in Table I.

Table I

Coating	D _{min}	D _{max}	Relative Speed
Example 1	0.36	1.0	140
Control 2	0.12	0.4	100

[0133] Note that after just 10 sec. of processing development Example Coating 1 provided a significantly higher D_{max} and photographic speed than Control Coating 2. This demonstrated the superiority of the redox amplification dye imaging process employing a color photographic element containing a high chloride {100} tabular grain emulsion.

EXAMPLE 2 Yellow monochrome layers

[0134] Emulsions 9, 10 and 11 were each optimally chemically and blue sensitized and then dual coated with an incorporated dispersion of a yellow dye forming coupler to give yellow single records suitable for redox amplification processing. The silver laydowns used are given in Table II. The prepared coatings were subject to sensitometric graduation exposures; exposure time of 0.1 sec with neutral density filter of 0.62 and a Wratten™ 98 filter. The coatings were processed in a redox amplification process using the redox amplifier formulation and process sequence given below.

Formulation for 1.0 liter of redox amplifier:	
1-hydroxyethylidene-1,1'-diphosphonic acid	0.6 g
diethyltriamine-pentaacetic acid	2.0 mL
K ₂ CO ₃	10.0 g
KBr	1.0 mg
KCl	0.35 g
Diethylhydroxylamine (85%)	4.0 mL
4-N-ethyl-N-(b-methanesulphonamidoethyl)-o-toluidine sesquisylphate	3.5 g
Water to	1000.0 mL
pH (27°C), adj with KOH to	10.3
Hydrogen peroxide	5.0 mL

Process sequence:	
Develop in an 8 liter tank 32°C	45 sec

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(continued)

Process sequence:	
Stop 15 g/L Na <i>meta</i> -bisulphite	30 sec
Bleach/Fix (Ektacolor RA4 TM)	30 sec
Wash	60 sec

[0135] The yellow wedges on the processed material were then read using a densitometer, and appropriate sensitometric parameters calculated. These are shown in Table II.

Table II

Emul	Silver (mg/m ²)	Grain Vol	Centers (10 ⁹)*	Dmin	Dmax	Contrast	Speed **
9	47.1	.270	52.2	.082	2.093	2.608	193
10	59.0	.422	33.4	.126	2.129	2.908	209
11	51.9	.292	45.9	.104	2.146	2.726	231

* No. of grains per square meter

** Speed was measured in this and subsequent Examples at the lowest perceptible density above Dmin

[0136] It can be seen that the high chloride {100} tabular grain Emulsion 11 produced a higher speed than either of the control cubic grain Emulsions 9 and 10, which were chosen to otherwise provide coating and performance parameters just above and just below those of Emulsion 11.

EXAMPLE 3 Yellow monochrome layers at lower silver laydown and greater amplification, with a fix only redox amplification process

[0137] Samples Emulsions 9, 10 and 11 as previously described were again employed. The silver laydowns used are given in the Table III. The prepared coatings were subject to sensitometric graduation exposures as described in Example 2. The coatings were processed in the same redox amplification process as for Example 2, but incorporating a Fix stage instead of a Bleach/Fix stage. To increase amplification, 60 secs. were used as the development time instead of 45 secs. The process sequence is outlined below.

Process sequence:	
Develop in an 8 liter tank 32°C	60 sec
Stop 15 g/L sodium <i>meta</i> -bisulphite	30 sec
Fix (Flexicolor TM C41)	30 sec
Wash	60 sec

[0138] The yellow wedges on the processed material were then read using a densitometer, and appropriate sensitometric parameters calculated. These are shown in Table III.

Table III

Emul	Silver (mg/m ²)	Grain Vol	Centers (10 ⁹)	Dmin	Dmax	Contrast	Speed
9	28.9	.270	32.1	.099	2.108	2.320	193
10	36.3	.422	20.5	.129	2.142	2.449	209
11	32.4	.292	28.6	.167	2.231	2.074	236
11	39.5	.292	35.0	.190	2.355	2.576	229

[0139] It can be seen that Emulsion 11 gave higher speed than that achieved with the Control Emulsions 9 and 10. A comparison of Control Emulsion 10 with the two levels of Emulsion 11 indicates higher Dmax and similar contrast. Thus an advantage has been maintained at reduced silver laydown (cf. also example 2), in a system in which developed silver has been retained in a dye image.

EXAMPLE 4 Multilayer

[0140] Six multilayer color photographic papers were coated similar to currently commercially available silver chloride colour paper. Samples of Control Emulsion 10 and Emulsion 11, prepared as described above, were used for the yellow dye image forming layer unit at the following silver laydowns (mg/m²): (Control Emulsion 10) 45.2, 64.6, 83.9; (Emulsion 11) 37.7, 53.8, 69.9. A conventional red sensitized cubic grain silver chloride emulsion of edge length 0.38 μm was used for the cyan dye image forming layer unit of these coatings at a silver laydown of 32.3 mg/m²; similarly a conventional green sensitized cubic grain silver chloride emulsion of edge length 0.31 micrometers was used for the magenta layer at a silver laydown of 37.7 mg/m².

[0141] A length of each color paper was exposed to a four color wedge (giving red, green, blue and neutral exposures) for 0.1 sec on a sensitometer, utilizing a filter pack containing a Wratten™ 2B plus 60M plus 60Y filters. The exposed coatings were then subjected to redox amplification using the formulation and process sequence shown below:

Formulation for 1.0 liter of redox amplifier:	
1-hydroxyethylidene-1,1'-diphosphonic acid	0.6 g
diethyltriamine-pentaacetic acid	2.0 mL
K ₂ CO ₃	25.0 g
KBr	1.0 mg
KCl	0.5 g
Diethylhydroxylamine (85%)	4.0 mL
Catechol disulfonate (Na)	0.60 g
4-N-ethyl-N-(β-methanesulfonamidoethyl)-o-toluidine sesquisulfate	3.5 g
Water to	1000 mL
pH (27°C), adj with KOH to	10.3
Hydrogen peroxide	5.0 mL

Process sequence:	
Drum Develop at 32°C	45 sec
Stop 2% acetic acid	30 sec
Wash	30 sec
Bleach/Fix (Ektacolor™ RA4)	30 sec
Wash	60 sec

[0142] The yellow separation wedges on the processed material were then read using a densitometer, and sensitometric parameters calculated. These are shown in the Table IV.

Table IV

Emulsion	Silver	Dmin	Dmax	Contrast*	Speed *	Speed **
10	45.2	.097	1.773	1.956	118	** 155
	64.6	.103	2.086	2.483	117	158
	83.9	.103	2.191	2.823	118	160
11	37.7	.106	1.936	1.98	152	192
	53.8	.115	2.197	2.449	154	195
	69.9	.124	2.238	2.87	156	199

* Yellow separation wedge.

** Neutral (unbalanced) wedge.

[0143] As observed in the monochrome examples, higher speed was obtained at constant contrast and lower silver laydown. For instance, compare the results for Control Emulsion 10 at a silver laydown of 83.9 mg/m² versus Emulsion C at a laydown of 69.9 mg/m².

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[0144] Because of the very high blue speed difference observed between the color paper containing the high chloride {100} tabular grain emulsion and the comparison color paper, the neutral images were not sufficiently balanced to allow a valid comparison of neutral sensitometric results. Exposure filtration was adjusted to give matching neutrals on three coatings (Control Emulsion 10 at 83.9 mg/m² silver, and Emulsion 11 at 53.8 and 69.9 mg/m²). The sensitometric parameters generated on these matching neutral wedges are shown in Table V.

Table V

Blue response in matched neutral (0.1 sec exposure)								
Emul	Ag	Dmin	Dmax	Cont.	Shoulder	Toe	Filtration*	Delta**
10	83.9	.117	2.441	3.145	1.816	.354	50Y+5M	0
11	53.8	.122	2.327	2.914	1.751	.390	105Y+5M	55Y
11	69.9	.124	2.378	3.145	1.822	.378	120Y	70Y-5M

* Kodak Color Compensating Filters

** Difference in filtration.

[0145] As observed previously, the higher speed (shown by higher yellow filtration needed to produce matched neutrals) is maintained at constant contrast and lower silver coating coverages when dye image amplification is taking place in yellow, magenta and cyan dye image forming layer units.

EXAMPLE 5 Comparison of retained silver in single color records and multilayers with a fix only process

[0146] Samples of the color papers compared in Table V, Control Emulsion 10 (83.9 mg/m² silver) and Emulsion 11 (69.9 mg/m²) were exposed and processed in a fix only process (the process sequence as shown in Example 4, except the Bleach/Fix stage was replaced by a sulfite fix). In this process the developed silver images were retained in the dye image forming layer units. It is possible to obtain a measure of the extent of yellow dye degradation caused by the retained silver by matching the wedges at a density of 2.0 (blue separation exposures in the case of multilayer examples) and measuring the unwanted red and green absorptions. These are shown in Table VI. A similar exercise was performed on the yellow single color records previously examined in Example 3, and the results are shown in Table VII.

Table VI

Multilayer data				
Emulsion	Ag	Yellow Separation	Yellow Separation	Yellow Separation
		Blue Density	Green Density	Red Density
10	83.9	2.0	0.53	0.25
11	69.9	2.0	0.52	0.25

Table VII

Yellow single color record data				
Emulsion	Silver (mg/m ²)	Blue Density	Green Density	Red Density
9	28.9	2.00	.43	.22
10	36.3	2.00	.45	.23
11	32.4	2.00	.45	.24
11	39.5	2.00	.45	.24

[0147] From Tables VI and VII very similar, especially red, unwanted absorptions were observed. This demonstrates that, contrary to expectations based on the reported higher covering power of tabular grain emulsions, no imaging penalty as compared to cubic grain emulsions resulted from retaining unbleached silver. Instead the speed advantage of the {100} tabular grain emulsion was obtained with no significant loss in dye image quality due to retained silver, when compared to the cubic grain emulsions.

Claims

- 5 1. A color photographic element containing a dye image forming layer unit comprised of at least one silver halide emulsion and a dye image providing compound
 CHARACTERIZED IN THAT
- total silver in the dye image forming layer unit is less than 200 mg/m² and
 the emulsion contains a silver halide grain population comprised of at least 50 mole percent chloride, based
10 on total silver forming the grain population, and greater than 30 percent of the grain population projected area
 is accounted for by tabular grains each having an aspect ratio of at least 2, a thickness of less than 0.3 μm,
 and parallel major faces lying in {100} crystallographic planes.
2. A color photographic element according to claim 1 further characterized in that greater than 50 percent of the grain
15 projected area is accounted for by the tabular grains.
3. A color photographic element according to claim 1 or 2 further characterized in that the tabular grains have a mean
 thickness of less than 0.2 μm.
4. A color photographic element according to any one of claims 1 to 3 inclusive further characterized in that the tabular
20 grains contain less than 2 mole percent iodide.
5. A color photographic element according to any one of claims 1 to 4 inclusive further characterized in that the dye
 image forming layer unit contains less than 133 mg/m² total silver.
- 25 6. A color photographic element according to claim 5 further characterized in that the dye image forming layer unit
 contains less than 110 mg/m² total silver.
7. A color photographic element according to claim 6 further characterized in that the dye image forming layer unit
30 contains less than 85 mg/m² total silver.
8. A color photographic element according to any one of claims 1 to 7 inclusive further characterized in that the
 photographic element is comprised of at least two dye image forming layer units and contains less than 400 mg/
 m² total silver.
- 35 9. A process of producing a dye image in an imagewise exposed color photographic element according to any one
 of claims 1 to 8 inclusive by developing the silver halide emulsion to produce silver imagewise and employing the
 developed silver to catalyze the reaction of an oxidizing agent and a reducing agent that are inert to oxidation-
 reduction interaction in the absence of developed silver, and reacting oxidized reducing agent with the dye image
40 providing compound to form the dye image.
10. A process according to claim 9 further characterized in that the dye image providing compound is a coupler, the
 reducing agent is a color developing agent, and the oxidizing agent is a peroxide or cobalt (III) complex.

45 **Patentansprüche**

1. Farbphotographisches Element, das eine ein Farbstoffbild erzeugende Schichteinheit enthält, welche mindestens
 eine Silberhalogenidemulsion und eine ein Farbstoffbild liefernde Verbindung umfaßt, dadurch gekennzeichnet,
50 daß
- Gesamt-Silber in der ein Farbstoffbild erzeugenden Schichteinheit geringer als 200 mg/m² ist und
 die Emulsion eine Silberhalogenid-Kornpopulation enthält, die mindestens 50 Molprozent Chlorid, bezogen
 auf Gesamt-Silber, welches die Kornpopulation bildet, umfaßt und tafelförmige Körner mit einem Durchmes-
55 ser-zu-Dicken-Verhältnis von mindestens 2, einer Dicke von weniger als 0,3 μm und parallelen Hauptflächen,
 die in kristallographischen {100}-Ebenen liegen, mehr als 30 Prozent der von der Kornpopulation projizierten
 Fläche ausmachen.
2. Farbphotographisches Element nach Anspruch 1, weiter dadurch gekennzeichnet, daß die tafelförmigen Körner

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mehr als 50 Prozent der von Korn projizierten Fläche ausmachen.

3. Farbphotographisches Element nach Anspruch 1 oder 2, weiter dadurch gekennzeichnet, daß die tafelförmigen Körner eine mittlere Dicke von weniger als $0,2 \mu\text{m}$ aufweisen.
4. Farbphotographisches Element nach irgendeinem der Ansprüche 1 bis 3 einschließlich, weiter dadurch gekennzeichnet, daß die tafelförmigen Körner weniger als 2 Molprozent Iodid enthalten.
5. Farbphotographisches Element nach irgendeinem der Ansprüche 1 bis 4 einschließlich, weiter dadurch gekennzeichnet, daß die ein Farbstoffbild erzeugende Schichteinheit weniger als 133 mg/m^2 Gesamt-Silber enthält.
6. Farbphotographisches Element nach Anspruch 5, weiter dadurch gekennzeichnet, daß die ein Farbstoffbild erzeugende Schichteinheit weniger als 110 mg/m^2 Gesamt-Silber enthält.
7. Farbphotographisches Element nach Anspruch 6, weiter dadurch gekennzeichnet, daß die ein Farbstoffbild erzeugende Schichteinheit weniger als 85 mg/m^2 Gesamt-Silber enthält.
8. Farbphotographisches Element nach irgendeinem der Ansprüche 1 bis 7 einschließlich, weiter dadurch gekennzeichnet, daß das photographische Element mindestens zwei ein Farbstoffbild erzeugende Schichteinheiten umfaßt und weniger als 400 mg/m^2 Gesamt-Silber enthält.
9. Verfahren zur Herstellung eines Farbstoffbildes in einem bildweise belichteten farbphotographischen Element nach irgendeinem der Ansprüche 1 bis 8 einschließlich durch Entwickeln der Silberhalogenidemulsion, um Silber bildweise zu erzeugen, und Verwenden des entwickelten Silbers, um die Reaktion eines Oxidationsmittels und eines Reduktionsmittels, die gegen eine Oxidations-Reduktions-Wechselwirkung in Abwesenheit von entwickeltem Silber inert sind, zu katalysieren, und Umsetzen von oxidiertem Reduktionsmittel mit der ein Farbstoffbild liefernden Verbindung unter Bildung des Farbstoffbildes.
10. Verfahren nach Anspruch 9, weiter dadurch gekennzeichnet, daß die ein Farbstoffbild liefernde Verbindung ein Kuppler ist, das Reduktionsmittel ein Farbentwicklungsmittel ist und das Oxidationsmittel ein Peroxid oder Cobalt (III)-Komplex ist.

Revendications

1. Élément photographique couleur contenant une unité de couches formatrices d'image de colorant comprenant au moins une émulsion aux halogénures d'argent et un composé formateur d'image de colorant
CARACTERISE EN CE QUE
l'argent total contenu dans l'unité de couches formatrices d'image de colorant est inférieur à 200 mg/m^2 et l'émulsion contient une population de grains d'halogénures d'argent comprenant au moins 50 pourcent en moles de chlorure, par rapport à l'argent total formant la population de grains, et plus de 30 pourcent de la surface projetée de la population de grains sont représentés par des grains tabulaires ayant chacun un indice de forme d'au moins 2, une épaisseur inférieure à $0,3 \mu\text{m}$ et des faces principales parallèles reposant dans des plans cristallographiques $\{100\}$.
2. Élément photographique couleur selon la revendication 1, caractérisé aussi en ce que plus de 50 pourcent de la surface projetée des grains sont représentés par des grains tabulaires.
3. Élément photographique couleur selon la revendication 1 ou 2, caractérisé aussi en ce que les grains tabulaires ont une épaisseur moyenne inférieure à $0,2 \mu\text{m}$.
4. Élément photographique couleur selon l'une quelconque des revendications 1 à 3 incluse, caractérisé aussi en ce que les grains tabulaires contiennent moins de 2 pourcent en moles d'iodure.
5. Élément photographique couleur selon l'une quelconque des revendications 1 à 4 incluse, caractérisé aussi en ce que l'unité de couches formatrices d'image de colorant contient moins de 133 mg/m^2 d'argent total.

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6. Élément photographique couleur selon la revendication 5, caractérisé aussi en ce que l'unité de couches formatrices d'image de colorant contient moins de 110 mg/m² d'argent total.

5 7. Élément photographique couleur selon la revendication 6, caractérisé aussi en ce que l'unité de couches formatrices d'image de colorant contient moins de 85 mg/m² d'argent total.

10 8. Élément photographique couleur selon l'une quelconque des revendications 1 à 7 incluse, caractérisé aussi en ce que l'élément photographique comprend au moins deux unités de couches formatrices d'image de colorant et contient moins de 400 mg/m² d'argent total.

15 9. Procédé de production d'une image de colorant dans un élément photographique exposé conformément à l'image, selon l'une quelconque des revendications 1 à 8 incluse, en développant l'émulsion aux halogénures d'argent afin de produire de l'argent conformément à l'image et en employant l'argent développé pour catalyser la réaction d'un agent oxydant et d'un agent réducteur qui sont inertes à l'interaction oxydation-réduction en l'absence d'argent développé, et en faisant réagir l'agent réducteur oxydé avec le composé formateur d'image de colorant pour former l'image de colorant.

20 10. Procédé selon la revendication 9, caractérisé aussi en ce que le composé formateur d'image de colorant est un coupleur, l'agent réducteur est un développeur chromogène et l'agent oxydant est un peroxyde ou un complexe de cobalt(III).

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