(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 617 322 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **94200681.8**

(22) Date of filing: **16.03.94**

(51) Int. Cl.[5]: **G03C 1/005**, G03C 7/392, G03C 7/413

(30) Priority: **22.03.93 US 35347**
09.02.94 US 193831

(43) Date of publication of application:
28.09.94 Bulletin 94/39

(84) Designated Contracting States:
DE FR GB

(71) Applicant: **EASTMAN KODAK COMPANY**
343 State Street
Rochester New York 14650-2201 (US)

(72) Inventor: **Brust, Thomas Brownell, c/o**
EASTMAN KODAK COMPANY
Patent Department,
343 State Street
Rochester, New York 14650-2201 (US)
Inventor: **Gould, Sharon, c/o EASTMAN**
KODAK COMPANY
Patent Department,
343 State Street
Rochester, New York 14650-2201 (US)
Inventor: **Sutton, James Edward, c/o**
EASTMAN KODAK COMPANY
Patent Department,
343 State Street
Rochester, New York 14650-2201 (US)
Inventor: **Szajewski, Richard P., c/o EASTMAN**
KODAK COMPANY
Patent Department,
343 State Street
Rochester, New York 14650-2201 (US)
Inventor: **Buchanan, John Michael, c/o**
EASTMAN KODAK COMPANY
Patent Department,
343 State Street
Rochester, New York 14650-2201 (US)

(74) Representative: **Nunney, Ronald Frederick**
Adolphe et al
Kodak Limited
Patent Department
Headstone Drive
Harrow Middlesex HA1 4TY (GB)

(54) **Method of processing originating photographic elements containing tabular silver chloride grains bounded by (100) faces.**

(57) A method of processing an exposed originating silver halide color photographic element comprising developing the photographic element in a color devoloper containing a p-phenylenediamine color developing agent in the presence of a 1-phenyl pyrazolidin-3-one compound

wherein the originating silver halide photographic element comprises a radiation sensitive emulsion in reactive association with a development inhibitor releasing compound and containing a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population projected area, wherein at least 50 percent of total grain projected area is accounted for by intrinsically stable tabular grains

(1) bounded by {100} major faces having adjacent edge ratios of less than 10 and

(2) each having an aspect ratio of at least 2, and wherein the silver halide content of the photographic element comprises at least 50 mole % silver chloride and no more than 2 mole % silver iodide.

EP 0 617 322 A1

FIG. 1

Field of the Invention

This invention relates to an improved processing method for developing and/or desilvering originating photographic elements and display photographic elements.

Background of the Invention

The basic image-forming process of color photography comprises exposing a silver halide photographic recording material to light, and chemically processing the material to reveal a useable image. The fundamental steps of this processing typically entail: (1) treating the exposed silver halide with a color developer wherein some or all of the silver halide is reduced to metallic silver while an organic dye is formed from the oxidized color developer; and (2) removing the silver metal thus formed and any residual silver halide by the desilvering steps of bleaching, wherein the developed silver is oxidized to silver salts, and fixing, wherein the silver salts are dissolved and removed from the photographic material. The bleaching and fixing steps may be performed sequentially or as a single step, which is discussed herein as blixing. In some methods of color image formation, additional color or black & white development steps, chemical fogging steps and ancillary stopping, washing, accelerating and stabilizing steps may be employed.

In many situations, the useable image is provided to a customer by a multi-stage method which involves exposing a light sensitive originating element to a scene, and developing and desilvering that originating element to form a color image. The originating element may, for example, be a color negative film or a motion picture negative film. The resultant color image is then used to modulate the exposure of a light sensitive display element, with optional enlargement, in a printer. The display element may, for example, be a color paper, an intermediate film, or a motion picture projection film. The exposed display element is then developed and desilvered to form a useful color image which duplicates the original scene.

Originating elements are typically designed to allow good exposure with available light under a wide variety of lighting conditions, that is, good sensitivity (speed/grain) and dynamic range (long latitude and low gamma) are desired. Conversely, display elements are typically designed so as to allow a full range of density formation after well defined exposure and process conditions in a printer, that is, good image discrimination (high density and low fog), low dynamic range (short latitude and high gamma) and easy and consistent processing are desired. These greatly different needs are typically met by providing originating and display elements that differ markedly in silver halide content and composition as well as in the layer orders and types and quantities of image forming chemicals employed in each. One major difference in composition is evidenced in the use of silver iodobromide emulsions in the originating element, a color negative film for example, for their high sensitivity and desirable image structure properties and the use of silver chloride or silver chlorobromide emulsions in the display element, a color paper for example, for their low sensitivity, short latitude and good developability, as well as their ease of reproducible desilvering.

Silver chloride emulsions are generally known for their rapid development properties. Once reduction of silver has started, the silver chloride will rapidly reduce to silver in most common photographic developers. The problem with silver chloride emulsions in originating elements has been that the initiation of development or the latent image detection that precedes the rapid development is slow, thus silver chloride emulsions tend to have low sensitivity with high gamma. While these characteristics are suitable for print materials, camera origination materials, as already noted, must be highly sensitive and have a long latitude with relatively low gamma such as a typical color negative film. Silver chloride emulsions can only achieve the low gamma and long latitude when they are developed for very short times or in very weak developers. These short development times do not appear to be sufficient to detect the latent image of the grains receiving the least exposure, thus the sensitivity is very low when the gamma and latitude are at the desired level.

What is needed is a method of developing high chloride silver halide originating photographic elements which takes advantage of the high speed development potential of silver chloride emulsions while still providing the sensitivity, gamma and latitude requirements of such an element.

Summary of the Invention

This invention provides a method of processing an exposed originating silver halide color photographic element comprising developing the photographic element in a color devoloper containing a p-phenylenediamine color developing agent, in the presence of a 1-phenyl pyrazolidin-3-one type compound;

wherein the originating silver halide photographic element comprises a radiation sensitive emulsion in

reactive association with a development inhibitor releasing compound and containing a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population projected area, wherein at least 50 percent of total grain projected area is accounted for by intrinsically stable tabular grains

(1) bounded by {100} major faces having adjacent edge ratios of less than 10 and

(2) each having an aspect ratio of at least 2, and wherein the silver halide content of the photographic element comprises at least 50 mole % silver chloride and no more than 2 mole % silver iodide.

The enhanced latent image detection provided by this invention allows the use of short development times and development inhibitor releasing couplers to produce a low gamma, long latitude imaging material while still maintaining high sensitivity. It further allows emulsions to rapidly achieve their maximum sensitivity before rapid and complete grain development takes place. The pyrazolidin compounds of this invention increase photographic speed as much as 0.6 log E for development times of 1 minute or less.

Development of silver chloride based films for short times or in weak developers has several added advantages such as rapid access and low replenishment rates leading to a more ecological process. The short development time and rapid latent image detection also allows development inhibitor releasing couplers to be more effective at reducing gamma and inducing interimage effects which can improve both color reproduction and sharpness.

Brief Description of the Figures

Figure 1 is a shadowed photomicrograph of carbon grain replicas of an emulsion of the invention and Figure 2 is a shadowed photomicrograph of carbon grain replicas of a control emulsion.

Detailed Description of the Invention

The originating silver halide photographic elements of this invention allow good exposure with available light under a wide variety of lighting conditions. They provide good speed with low graininess. At a minimum the originating elements of this invention have an ISO speed rating of 25 or greater, with greater than 50 being preferred.

The speed or sensitivity of color negative photographic materials is inversely related to the exposure required to enable the attainment of a specified density above fog after processing. Photographic speed for color negative films with a gamma of about 0.65 has been specifically defined by the American National Standards Institute (ANSI) as ANSI Standard Number PH 2.27 - 1979 (ASA speed) and relates to the exposure levels required to enable a density of 0.15 above fog in the green light sensitive and least sensitive recording unit of a multicolor negative film. This definition conforms to the International Standards Organization (ISO) film speed rating.

It is appreciated that according to the above definition, speed depends on film gamma. Color negative films intended for other than direct optical printing may be formulated or processed to achieve a gamma greater or less than 0.65. For the purposes of this application, the speeds of such films are determined by first linearly amplifying or deamplifying the achieved density vs log exposure relationship (i.e. the gamma) to a value of 0.65 and then determining the speed according to the above definitions.

The photographic emulsions used in the originating element may include, among others, silver chloride, silver bromochloride, silver bromide, silver iodobromochloride, silver iodochloride or silver iodobromide. Silver chloride and silver bromochloride emulsions are preferred. Whatever the emulsion mix, the originating photographic element must contain at least about 50 mole % silver chloride, with 70 mole % being preferrred and over 98 mole % being most preferred. The total amount of silver iodide in the photographic element must be less than about 2 mole %, and preferrably less than 1 mole %. The total amount of coated silver may be from about 1 to about 10 grams per square meter, with less than 7 grams per square meter preferred, and less than 4 grams per square meter being most preferred.

The originating photographic elements of this invention contain at least one radiation sensitive silver halide emulsion containing a dispersing agent and a high chloride silver halide grain population. At least 50 percent of total grain projected area of the high chloride grain population is accounted for by tabular grains which (1) are bounded by {100} major faces having adjacent edge ratios of less than 10 and (2) each have an aspect ration of at least 2. The tabular grains of this invention are intrinsically stable and do not require the use of stabilizers such as thiirane, thiepine, thiophene, thiazole and other such cyclic sulfides; mercaptoacetic acids, cysteine, penicillamine and other thiols; and acetylthiophenol and related thioesters and thiocarbanimides to maintain their shape. Such stabilizers may restrain development.

It has further been discovered that the use of a certain class of development inhibitors can inhibit the desilvering of the originating photographic elements of this invention. Development inhibitors typically comprise a silver halide binding group having a sulfur, selenium, tellurium or heterocyclic nitrogen or carbon with a free valence that can form a bond to silver atoms, as well as a ballast moiety. Originating photographic elements which contain development inhibitors having a sulfur with a free valence that can form a bond to a silver atom appear to desilver more slowly than those containing other classes of development inhibitors or no development inhibitor. Therefore, with this invention it is preferred to use development inhibitors with a heterocyclic nitrogen as a silver binding group, such as oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles, benzotriazoles, tetrazoles, benzimidazoles, indazoles, isoindazoles, benzodiazolesor benzisodiazoles. Development inhibitors having a sulfur with a free valence can, however, have other advantages and may be utilized in limited quantities which do not greatly effect desilvering.

The identification of emulsions satisfying the requirements of the invention and the significance of the selection parameters can be better appreciated by considering a typical emulsion. Figure 1 is a shadowed photomicrograph of carbon grain replicas of a representative emulsion of the invention, described in detail in Example 1 below. It is immediately apparent that most of the grains have orthogonal tetragonal (square or rectangular) faces. The orthogonal tetragonal shape of the grain faces indicates that they are {100} crystal faces.

The projected areas of the few grains in the sample that do not have square or rectangular faces are noted for inclusion in the calculation of the total grain projected area, but these grains clearly are not part of the tabular grain population having {100} major faces.

A few grains may be observed that are acicular or rod-like grains (hereinafter referred as rods). These grains are more than 10 times longer in one dimension than in any other dimension and can be excluded from the desired tabular grain population based on their high ratio of edge lengths. The projected area accounted for by the rods is low, but, when rods are present, their projected area is noted for determining total grain projected area.

The grains remaining all have square or rectangular major faces, indicative of {100} crystal faces. To identify the tabular grains it is necessary to determine for each grain its ratio of ECD to thickness (t)-i.e., ECD/t. ECD is determined by measuring the projected area (the product of edge lengths) of the upper surface of each grain. From the grain projected area the ECD of the grain is calculated. Grain thickness is commonly determined by oblique illumination of the grain population resulting in the individual grains casting shadows. From a knowledge of the angle of illumination (the shadow angle) it is possible to calculate the thickness of a grain from a measurement of its shadow length. The grains having square or rectangular faces and each having a ratio of ECD/t of at least 2 are tabular grains having {100} major faces. When the projected areas of the {100} tabular grains account for at least 50 percent of total grain projected area, the emulsion is a tabular grain emulsion.

In the emulsion of Figure 1 tabular grains account for more than 50 percent of total grain projected area. From the definition of a tabular grain above, it is apparent that the average aspect ratio of the tabular grains can only approach 2 a minimum limit. In fact, tabular grain emulsions of the invention typically exhibit average aspect ratios of 5 or more, with high average aspect ratios (>8) being preferred. That is, preferred emulsions according to the invention are high aspect ratio tabular grain emulsions. In specifically preferred emulsions according to the invention average aspect ratios of the tabular grain population are at least 12 and optimally at least 20. Typically the average aspect ratio of the tabular grain population ranges up to 50, but higher aspect ratios of 100, 200 or more can be realized. Emulsions within the contemplation of the invention in which the average aspect ratio approaches the minimum average aspect ratio limit of 2 still provide a surface to volume ratio that is 200 percent that of cubic grains.

The tabular grain population can exhibit any grain thickness that is compatible with the average aspect ratios noted above. However, particularly when the selected tabular grain population exhibits a high average aspect ratio, it is preferred to additionally limit the grains included in the selected tabular grain population to those that exhibit a thickness of less than 0.3 μm and, optimally, less than 0.2 μm. It is appreciated that the aspect ratio of a tabular grain can be limited either by limiting its equivalent circular diameter or increasing its thickness. Thus, when the average aspect ratio of the tabular grain population is in the range of from 2 to 8, the tabular grains accounting for at least 50 percent of total grain projected area can also each exhibit a grain thickness of less than 0.3 μm or less than 0.2 μm. Nevertheless, in the aspect ratio range of from 2 to 8 particularly, there are specific photographic applications that can benefit by greater tabular grain thicknesses. For example, in constructing a blue recording emulsion layer of maximum achievable speed it is specifically contemplated that tabular grain thicknesses that are on average 1 μm or or even larger can be tolerated. This is because the eye is least sensitive to the blue record and hence higher levels of image

granularity (noise) can be tolerated without objection. There is an additional incentive for employing larger grains in the blue record in that it is sometimes difficult to match in the blue record the highest speeds attainable in the green and red record. A source of this difficulty resides in the blue photon deficiency of sunlight. While sunlight on an energy basis exhibits equal parts of blue, green and red light, at shorter wavelengths the photons have higher energy. Hence on a photon distribution basis daylight is slightly blue deficient.

The tabular grain population preferably exhibits major face edge length ratios of less than 5 and optimally less than 2. The nearer the major face edge length ratios approach 1 (i.e., equal edge lengths) the lower is the probability of a significant rod population being present in the emulsion. Further, it is believed that tabular grains with lower edge ratios are less susceptible to pressure desensitization.

In one specifically preferred form of the invention the tabular grain population accounting for at least 50 percent of total grain projected area is provided by tabular grains also exhibiting 0.2 μm. In other words, the emulsions are in this instance thin tabular grain emulsions.

Surprisingly, ultrathin tabular grain emulsions have been prepared satisfying the requirements of the invention. Ultrathin tabular grain emulsions are those in which the selected tabular grain population is made up of tabular grains having an average thickness of less than 0.06 μm. Prior to the present invention the only ultrathin tabular grain emulsions of a halide content exhibiting a cubic crystal lattice structure known in the art contained tabular grains bounded by {111} major faces. In other words, it was thought essential to form tabular grains by the mechanism of parallel twin plane incorporation to achieve ultrathin dimensions. Emulsions according to the invention can be prepared in which the tabular grain population has a mean thickness down to 0.02 μm and even 0.01 μm. Ultrathin tabular grains have extremely high surface to volume ratios. This permits ultrathin grains to be photographically processed at accelerated rates. Further, when spectrally sensitized, ultrathin tabular grains exhibit very high ratios of speed in the spectral region of sensitization as compared to the spectral region of native sensitivity. For example, ultrathin tabular grain emulsions according to the invention can have entirely negligible levels of blue sensitivity, and are therefore capable of providing a green or red record in a photographic product that exhibits minimal blue contamination even when located to receive blue light.

The characteristic of tabular grain emulsions that sets them apart from other emulsions is the ratio of grain ECD to thickness (t). This relationship has been expressed quantitatively in terms of aspect ratio. Another quantification that is believed to assess more accurately the importance of tabular grain thickness is tabularity:

$$T = ECD/t^2 = AR/t$$

where

T is tabularity;

AR is aspect ratio;

ECD is equivalent circular diameter in micrometers (μm); and

t is grain thickness in micrometers.

The high chloride tabular grain population accounting for 50 percent of total grain projected area preferably exhibits a tabularity of greater than 25 and most preferably greater than 100. Since the tabular grain population can be ultrathin, it is apparent that extremely high tabularities, ranging to 1000 and above are within the contemplation of the invention.

The tabular grain population can exhibit an average ECD of any photographically useful magnitude. For photographic utility average ECD's of less than 10 μm are contemplated, although average ECD's in most photographic applications rarely exceed 6 μm. Within ultrathin tabular grain emulsions satisfying the requirements of the invention it is possible to provide intermediate aspect ratios with ECD's of the tabular grain population of 0.10 μm and less. As is generally understood by those skilled in the art, emulsions with selected tabular grain populations having higher ECD's are advantageous for achieving relatively high levels of photographic sensitivity while selected tabular grain populations with lower ECD's are advantageous in achieving low levels of granularity.

So long as the population of tabular grains satisfying the parameters noted above accounts for at least 50 percent of total grain projected area a photographically desirable grain population is available. It is recognized that the advantageous properties of the emulsions of the invention are increased as the proportion of tabular grains having {100} major faces is increased. The preferred emulsions according to the invention are those in which at least 70 percent and optimally at least 90 percent of total grain projected area is accounted for by tabular grains having {100} major faces. It is specifically contemplated to provide emulsions satisfying the grain descriptions above in which the selection of the rank ordered tabular grains

extends to sufficient tabular grains to account for 70 percent or even 90 percent of total grain projected area.

So long as tabular grains having the desired characteristics described above account for the requisite proportion of the total grain projected area, the remainder of the total grain projected area can be accounted for by any combination of coprecipitated grains. It is, of course, common practice in the art to blend emulsions to achieve specific photographic objectives. Blended emulsions in which at least one component emulsion satisfies the tabular grain descriptions above are specifically contemplated.

If tabular grains failing to satisfy the tabular grain population requirements do not account for 50 percent of the total grain projected area, the emulsion does not satisfy the requirements of the invention and is, in general, a photographically inferior emulsion. For most applications (particularly applications that require spectral sensitization, require rapid processing and/or seek to minimize silver coverages) emulsions are photographically inferior in which many or all of the tabular grains are relatively thick-e.g., emulsions containing high proportions of tabular grains with thicknesses in excess of 0.3 μm.

More commonly, inferior emulsions failing to satisfy the requirements of the invention have an excessive proportion of total grain projected area accounted for by cubes, twinned nontabular grains, and rods. Such an emulsion is shown in Figure 2. Most of the grain projected area is accounted for by cubic grains. Also the rod population is much more pronounced than in Figure 1. A few tabular grains are present, but they account for only a minor portion of total grain projected area.

The tabular grain emulsion of Figure 1 satisfying the requirements of the invention and the predominantly cubic grain emulsion of Figure 2 were prepared under conditions that were identical, except for iodide management during nucleation. The Figure 2 emulsion is a silver chloride emulsion while the emulsion of Figure 1 additionally includes a small amount of iodide.

Obtaining emulsions satisfying the requirements of the invention has been achieved by the discovery of a novel precipitation process. 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.

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 screw dislocations in one or more of the cubic crystal faces. The cubic crystal faces that contain at least one screw dislocation thereafter accept silver halide at an accelerated rate as compared to the regular cubic crystal faces (i.e., those lacking a screw dislocation). When only one of the cubic crystal faces contains a screw dislocation, 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 screw dislocations. However, when any two contiguous cubic crystal faces contain a screw dislocation, continued growth accelerates growth on both faces and produces a tabular grain structure. It is believed that the tabular grains of the emulsions of this invention are produced by those grain nuclei having two, three or four faces containing screw dislocations.

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.

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.

In the preferred form of the invention 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.

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.

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.

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 above 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.

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 hydrochloride 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.

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*, Vol. 308, December 1989, Item 308119, Section IX. *Research Disclosure* is published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire P010 7DD, England. 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 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. 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.

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.

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.

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 above.

In its simplest form the process of preparing emulsions according to the invention 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.

It is usually preferred to prepare photographic emulsions with the most geometrically uniform grain populations attainable, since this allows a higher percentage of the total 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.

In the preparation of emulsions according to the invention 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 above 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.

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 total grain 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 and thiocyanates. Typical thiocyanate ripening agents are disclosed by Nietz et al., U.S. Patent 2,222,264; Lowe et al., U.S. Patent 2,448,534; and Illingsworth, U.S. Patent 3,320,069, the disclosures of which are here incorporated by reference. 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, the disclosures of which are here incorporated by reference. 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 also been demonstrated to be effective in increasing the percentage of total grain projected accounted by the {100} tabular grains.

Once the desired population of grain nuclei have been formed, grain growth to obtain the emulsions of the invention 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 chloride 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.

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.

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; Teitschied et al., European Patent Application 80102242; 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*.

In the simplest form of the invention 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 above. 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, here incorporated by reference. In these arrangements the contents of the growth reaction vessel are recirculated to the nucleation reaction vessel.

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 0 368 275, Urabe et al., published European Patent Application 0 374 954, and Onishi et al., published Japanese Patent Application (Kokai) 172,817-A (1990).

Although the process of grain nucleation has been described above in terms of utilizing iodide to produce the crystal irregularities required for tabular grain formation, alternative nucleation procedures have been devised, demonstrated in the Examples below, 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 product tabular grains.

It has been observed that rapid grain nucleations, including so-called dump nucleations, in which significant levels of dispersing medium supersaturation 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 above are entirely consistent with this approach.

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 of 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.

The emulsions of the invention include silver chloride, silver iodochloride emulsions, silver iodobromochloride emulsions and silver iodochlorobromide emulsions. 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.

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, the disclosures of which are here incorporated by reference. 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 0 264 288.

The invention is particularly advantageous in providing high chloride (greater than 50 mole percent chloride) tabular grain emulsions, since conventional high chloride tabular grain emulsions having tabular grains bounded by {111} are inherently unstable and require the presence of a morphological stabilizer to prevent the grains from regressing to nontabular forms. Particularly preferred high chloride emulsions are according to the invention that are those that contain more than 70 mole percent (optimally more than 90 mole percent) chloride.

Although not essential to the practice of the invention, a further procedure that can be employed to maximize the population of tabular grains having {100} major faces 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.

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

Aromatic resonance can be relied upon for stabilization of the p 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.

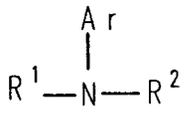
In one preferred form the restraining agent can satisfy the following formula:

(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.

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

R^1 and R^2 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, pyrrolidinyl, piperidinyl, furanyl and similar heterocyclic rings are specifically contemplated.

The following are representative of compounds contemplated satisfying formulae I and/or II: aniline, a-naphthylamine, b-naphthylamine, benzidine, carbazole, norharman, pyrrole, indole, pyridine, quinoline, isoquinoline, acridine, 1,8-naphthyridine, 1,10-phenanthroline, nicotine, benzoxazole, pyrazole, antipyrine, imidazole, indazole, pyrimidine, pyrazine, 2,2'-bipyrazine, pteridine, 1,2,3-triazole, 1,2,4-triazole, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, benzotriazole, 1,2,4-triazine, and 1,3,5-triazine.

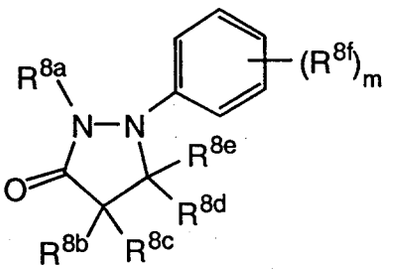
Selection of preferred restraining agents and their useful concentrations can be accomplished by the following selection procedure: The compound being considered for use as a restraining agent is added to a silver chloride emulsion consisting essentially of cubic grains with a mean grain edge length 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.

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

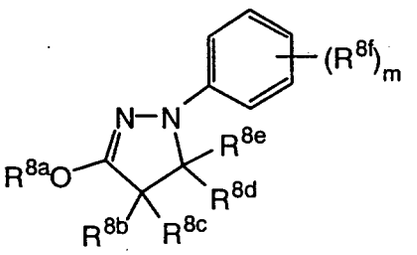
published applications (Kokai) 252649-A (priority 02.03.90-JP 051165 Japan) and 288143-A (priority 04.04.90-JP 089380 Japan). The disclosures of the above U.S. Patents are hereby incorporated by reference.

While any 1-phenyl pyrazolidin-3-one type compound may be used with this invention, the more preferred compounds have the following Formulas I or II.

Formula I



Formula II



wherein:

R^{8a} is hydrogen;

R^{8b} and R^{8c} each independently represent a hydrogen, a substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms or a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms;

R^{8d} and R^{8e} each independently represent a hydrogen, a substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms or a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms; and

R^{8f} is independently a hydrogen, a halogen, a substituted or unsubstituted alkyl group having from 1 to 8 carbon atoms, or a substituted or unsubstituted alkoxy group having from 1 to 8 carbon atoms, or a sulfonamido group. R^{8f} may be present in the ortho, meta or para positions of the benzene ring. m is 1 to 3. When m is greater than 1, the R^{8f} substituents can be taken together to form a carbocyclic or a heterocyclic ring.

More preferably m is 2; the R^{8f} substituents are in the para and meta positions of the benzene ring and each is a hydrogen or an alkoxy group having 1-4 carbon atoms, and R^{8b} and R^{8c} are each hydrogen or an alkyl group having 1-10 carbon atoms; provided that one of R^{8f} is an alkoxy group or one of R^{8b} and R^{8c} is an alkyl group of 3-7 carbon atoms. Preferably at least one R^{8f} is an alkoxy group of 1-4 carbon atoms, R^{8b} is hydrogen or an alkyl group of 1-4 carbon atoms, and R^{8c} is hydrogen or a hydroxyalkyl group of 1-4 carbon atoms. The preferred compounds for use are: 1-(4-methoxyphenyl)-3-pyrazolidone, 1-(3,4-dimethoxyphenyl)-3-pyrazolidone, and 1-phenyl-4-n-pentylpryazolidone, with 1-(4-methoxyphenyl)-3-pyrazolidone being most preferred.

The 1-phenyl pyrazolidin-3-one type compound may be present in the developer solution at a concentration up to 5 g/l preferably in the range 0.05 to 0.5 g/l. It may also be incorporated in the photographic element. When incorporated in the photographic material it may be present in one or more layers thereof. When the compound is incorporated in the photographic material, preferably it is in a form which is inactive until processing takes place. For example, it could be inactivated by a blocking group which is hydrolysed off when the material is immersed in the normally alkaline developing solution. The compound could also be released from a coupler as a function of silver halide development.

Any developer which is suitable for use with low iodide, chloride containing elements may be utilized with this invention. The color developing agent is a p-phenylenediamine. The content of the color developing agent is generally 1 to 30 grams per liter of the color developing solution, with 2 to 20 grams being more preferred and 3 to 10 grams being most preferred.

Examples of particularly useful p-phenylenediamines and especially the N-N-dialkyl-p-phenylenediamines in which the alkyl groups or the aromatic nucleus can be substituted or unsubstituted include: N-N-diethyl-p-phenylenediaminemonohydrochloride, 4-N,N-diethyl-2-methyl-phenylenediaminemonohydrochloride, 4-(N-ethyl-N-2-methanesulfonylaminoethyl)-2-methyl-phenylenediamine sesquisulfate monohydrate, 4-(N-ethyl-N-2-hydroxyethyl)-2-methylphenylenediamine sulfate, and 4-N, N-diethyl-2, 2'-methanesulfonylaminoethylphenylenediamine hydrochloride.

In addition to the primary aromatic amino color developing agent, the color developing solutions used with this invention may contain a variety of other agents such as alkalies to control pH, bromides, iodides, benzyl alcohol, anti-oxidants, anti-foggants, solubilizing agents, brightening agents, and so forth.

The photographic color developing compositions may be employed in the form of aqueous alkaline working solutions having a pH of above 7 and more preferably in the range of from about 9 to about 13. To provide the necessary pH, they may contain one or more of the well known and widely used pH buffering agents, such as the alkali metal carbonates or phosphates. Potassium carbonate is especially preferred.

The originating element is desilvered after color development is performed. Desilvering can be performed by one of the following methods (i) a method using a bleaching solution bath and fixing solution bath; (ii) a method using a bleaching solution bath and a blixing solution bath; (iii) a method using a blixing solution and a fixing solution bath; and (iv) a method using a single blixing bath. Blixing may be preferred in order to shorten the process time.

Examples of bleaching agents which may be used in the bleach solutions or blix solutions of the current invention are ferric salts, persulfate, dichromate, bromate, red prussiate, and salts of aminopolycaroxylic acid ferric complexes, with salts of aminopolycaroxylic acid ferric complexes being preferred.

Preferred aminopolycarboxylic acid ferric complexes are listed below:

(1) ethylenediaminetetraacetic acid ferric complex;
(2) diethylenetriaminepentaacetic acid ferric complex;
(3) cyclohexanediaminetetraacetic acid ferric complex;
(4) iminodiacetic acid ferric complex;
(5) methyliminodiacetic acid ferric complex;
(6) 1,3-diaminopropanetetraacetic acid ferric complex;
(7) glycoletherdiaminetetraacetic acid ferric complex;
(8) beta-alanine diacetic acid ferric complex.

These aminopolycarboxylic acid ferric complexes are used in the form of a sodium salt, potassium salt, or ammonium salt. An ammonium salt may be preferred for speed, with alkali salts being preferred for environmental reasons.

The content of the salt of an aminopolycarboxylic acid ferric complex in the bleaching solutions and blixing solutions of this invention is about 0.05 to 1 mol/liter. The pH range of the bleaching solution is 2.5 to 7, and preferably 4.0 to 7.

The bleaching solution or the blixing solution can contain rehalogenating agents such as bromides (e.g., potassium bromide, sodium bromide, and ammonium bromide), chlorides (e.g., potassium chloride, sodium chloride, and ammonium chloride), and iodides (e.g., ammonium iodide). They may also contain one or more inorganic and organic acids or alkali metal or ammonium salts thereof, and, have a pH buffer such as boric acid, borax, sodium methabrate, acetic acid, sodium acetate, sodium carbonate, potassium carbonate, phosphorous acid, phosphoric acid, sodium phosphate, citric acid, sodium citrate, and tartaric acid, or corrosion inhibitors such as ammonium mitrate and guanidine.

Examples of fixing agents which may be used in the this invention are water-soluble solvents for silver halide such as: a thiosulfate (e.g., sodium thiosulfate and ammonium thiosulfate); a thiocyanate (e.g., sodium thiocyanate and ammonium thiocyanate); a thioether compound (e.g., ethylenebisthioglycolic acid and 3,6-dithia-1,8-octanediole); and a thiourea. These fixing agents can be used singly or in a combination of at least two agents. Thiosulfate is preferably used in the present invention.

The content of the fixing agent per liter is preferably about 0.2 to 2 mol. The pH range of the blixing or fixing solution is preferably 3 to 10 and more preferably 5 to 9.

In order to adjust the pH of the fixing solution, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, bicarbonate, ammonia, potassium hydroxide, sodium hydroxide, sodium carbonate, potassium carbonate,may be added.

The blixing and the fixing solution may also contain a preservative such as a sulfite (e.g., sodium sulfite, potassium sulfite, and ammonium sulfite), a bisulfite (e.g., ammonium bisulfite, sodium bisulfite, and potassium bisulfite), and a metabisulfite (e.g., potassium metabisulfite, sodium metabisulfite, and ammonium metabisulfite). The content of these compounds is about 0 to 0.50 mol/liter, and more preferably 0.02 to 0.40 mol/liter as an amount of sulfite ion. Ascorbic acid, a carbonyl bisulfite, acid adduct, or a carbonyl

compound may also be used as a preservative.

It is known to those skilled in the art that numerous other auxillary processing steps are often used including washing, stabilizing, rinsing, reversal processing and neutralization. All of these processing steps may be utilized with the photographic elements of this invention.

Apart from the features that have been specifically discussed previously for the tabular grain emulsion preparation procedures and the tabular grains that they produce, their further use in the color photographic elements of this invention can take any convenient conventional form. Substitution in color photographic elements for conventional emulsions of the same or similar silver halide composition is generally contemplated, with substitution for silver halide emulsions of differing halide composition, particularly other tabular grain emulsions, being also feasible. The low levels of native blue sensitivity of the high chloride {100} tabular grain emulsions allows the emulsions to be employed in any desired layer order arrangement in multicolor photographic elements, including any of the layer order arrangements disclosed by Kofron et al., U.S. Patent 4,439,520, the disclosure of which is here incorporated by reference, both for layer order arrangements and for other conventional features of photographic elements containing tabular grain emulsions. Conventional features are further illustrated by the following incorporated by reference disclosures:

ICBR-1	*Research Disclosure*, Vol. 308, December, 1989, Item 308,119;
ICBR-2	*Research Disclosure*, Vol. 225, January, 1983, Item 22,534;
ICBR-3	Wey et al., U.S. Patent 4,414,306, issued Nov. 8, 1983;
ICBR-4	Solberg et al., U.S. Patent 4,433,048, issued Feb. 21, 1984;
ICBR-5	Wilgus et al., U.S. Patent 4,434,226, issued Feb. 28, 1984;
ICBR-6	Maskasky, U.S: Patent 4,435,501, issued Mar. 6, 1984;
ICBR-7	Maskasky, U.S. Patent 4,643,966, issued Feb. 17, 1987;
ICBR-8	Daubendiek et al., U.S. Patent 4,672,027, issued Jan. 9, 1987;
ICBR-9	Daubendiek et al., U.S. Patent 4,693,964, issued Sept. 15, 1987;
ICBR-10	Maskasky, U.S. Patent 4,713,320, issued Dec. 15, 1987;
ICBR-11	Saitou et al., U.S. Patent 4,797,354, issued Jan. 10, 1989;
ICBR-12	Ikeda et al., U.S. Patent 4,806,461, issued Feb. 21, 1989;
ICBR-13	Makino et al., U.S. Patent 4,853,322, issued Aug. 1, 1989; and
ICBR-14	Daubendiek et al., U.S. Patent 4,914,014, issued Apr. 3, 1990.

Photographically useful group (PUG)-releasing compounds can be incorporated in photographic elements of the present invention by means and processes known in the photographic art. A photographic element in which the dye image-forming and PUG-releasing compounds are incorporated can be a monocolor element comprising a support and a single silver halide emulsion layer, or it can be a multicolor, multilayer element comprising a support and multiple silver halide emulsion layers. The above described compounds can be incorporated in at least one of the silver halide emulsion layers and/or in at least one other layer, such as an adjacent layer, where they are in reactive association with the silver halide emulsion layer and are thereby able to react with the oxidized developing agent produced by development of silver halide in the emulsion layer. Additionally, the silver halide emulsion layers and other layers of the photographic element can contain addenda conventionally contained in such layers.

A typical multicolor, multilayer photographic element can comprise a support having thereon a red-sensitized silver halide emulsion unit having associated therewith a cyan dye image-forming compound, a green-sensitized silver halide emulsion unit having associated therewith a magenta dye image-forming compound, and a blue-sensitized silver halide emulsion unit having associated therewith a yellow dye image-forming compound. Each silver halide emulsion unit can be composed of one or more layers, and the various units and layers can be arranged in different locations with respect to one another, as known in the prior art and as illustrated by layer order formats hereinafter described.

In an element of the invention, a layer or unit affected by PUG can be controlled by incorporating in appropriate locations in the element a layer that confines the action of PUG to the desired layer or unit. Thus, at least one of the layers of the photographic element can be, for example, a scavenger layer, a mordant layer, or a barrier layer. Examples of such layers are described in, for example, U.S. Patents 4,055,429; 4,317,892; 4,504,569; 4,865,946; and 5,006,451. The element can also contain additional layers such as antihalation layers, filter layers and the like. The element typically will have a total thickness, excluding the support, of from 5 to 30 m. Thinner formulations of 5 to about 25 m are generally preferred since these are known to provide improved contact with the process solutions. For the same reason, more swellable film structures are likewise preferred. Further, this invention may be particularly useful with a magnetic recording layer such as those described in *Research Disclosure*, Item 34390, November, 1992, p. 869.

In the following discussion of suitable materials for use in the elements of this invention, reference will be made to the previously mentioned *Research Disclosure*, December, 1989, Item 308119, the disclosures of which are incorporated herein by reference.

Suitable dispersing media for the emulsion layers and other layers of elements of this invention are described in Section IX of *Research Disclosure*, December, 1989, Item 308119, and publications therein.

In addition to the compounds described herein, the elements of this invention can include additional dye image-forming compounds, as described in Sections VII A-E and H, and additional PUG-releasing compounds, as described in Sections VII F and G of *Research Disclosure*, December, 1989, Item 308119, and the publications cited therein.

The elements of this invention can contain brighteners (Section V), antifoggants and stabilizers (Section VI), antistain agents and image dye stabilizers (Section VII I and J), light absorbing and scattering materials (Section VIII), hardeners (Section X), coating aids (Section XI), plasticizers and lubricants (Section XII), antistatic agents (Section XIII), matting agents (Section XVI), and development modifiers (Section XXI), all in *Research Disclosure*, December, 1989, Item 308119.

The elements of the invention can be coated on a variety of supports, as described in Section XVII of *Research Disclosure*, December, 1989, Item 308119, and references cited therein.

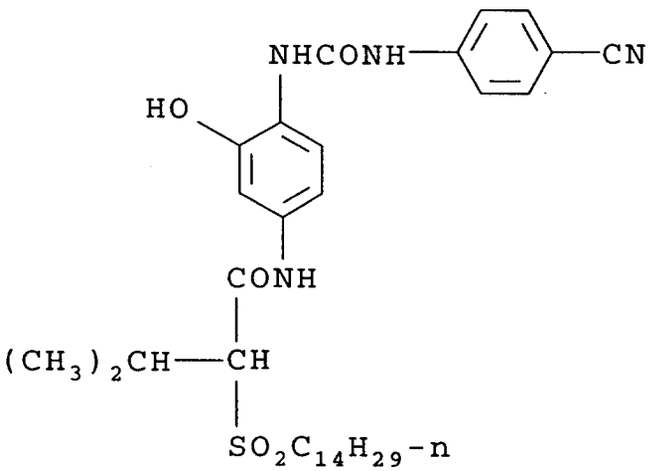
The photographic elements containing radiation sensitive {100} tabular grain emulsion layers according to this invention can be imagewise-exposed with various forms of energy which encompass the ultraviolet and visible (e.g., actinic) and infrared regions of the electromagnetic spectrum, as well as electron-beam and beta radiation, gamma ray, X-ray, alpha particle, neutron radiation and other forms of corpuscular and wave-like radiant energy in either noncoherent (random phase) forms or coherent (in phase) forms as produced by lasers. Exposures can be monochromatic, orthochromatic or panchromatic. Imagewise exposures at ambient, elevated or reduced temperatures and/or pressures, including high- or low-intensity exposures, continuous or intermittent exposures, exposure times ranging from minutes to relatively short durations in the millisecond to microsecond range and solarizing exposures, can be employed within the useful response ranges determined by conventional sensitometric techniques, as illustrated by T. H. James, The *Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapters 4, 6, 17, 18 and 23. The photographic elements may then be processed to form a visible dye image, as described in Sections XVIII and XIX of *Research Disclosure*, December, 1989, Item 308119.

The following examples are intended to illustrate, without limiting, this invention.

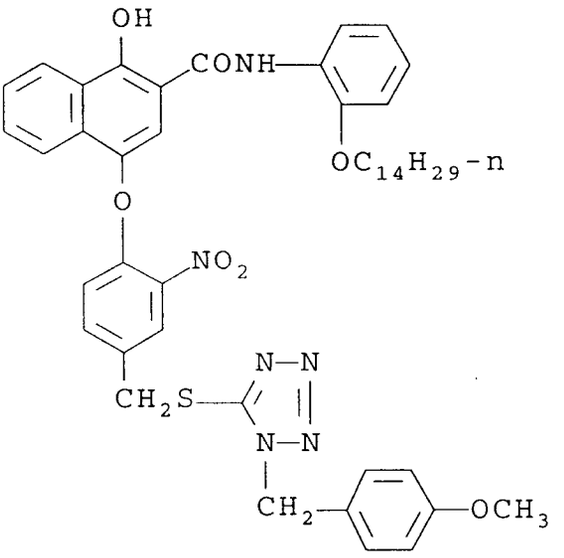
Examples

The invention can be better appreciated by reference to the following examples. Throughout the examples the acronym APMT is employed to designate 1-(3-acetamidophenyl)-5-mercaptotetrazole. The term "low methionine gelatin" is employed, except as otherwise indicated, to designate gelatin that has been treated with an oxidizing agent to reduce its methionine content to less than 30 micromoles per gram. The acronym DW is employed to indicate distilled water. The acronym mppm is employed to indicate molar parts per million.

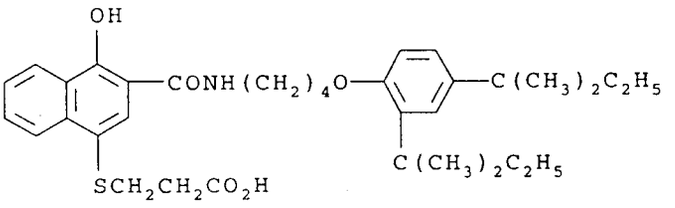
The following compounds are used in the Examples.



C-31

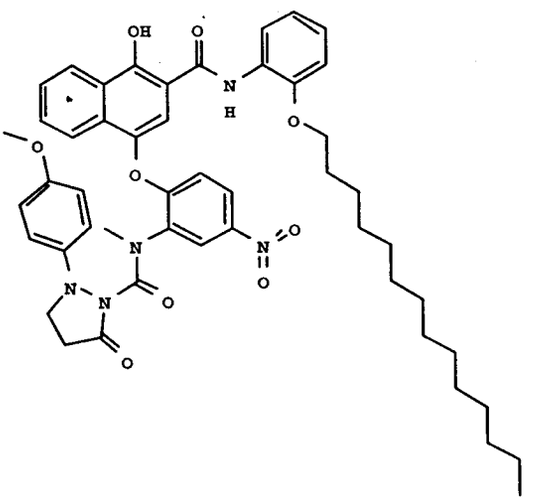


D-3



Bleach Accelerator

B-1



Electron Transfer Agent

C-52

Emulsion Preparation Example 1

This example demonstrates the preparation of an ultrathin tabular grain silver iodochloride emulsion satisfying the requirements of this invention.

A 2030 mL solution containing 1.75% by weight low methionine gelatin, 0.011 M sodium chloride and 1.48 x 10^{-4} M potassium iodide was provided in a stirred reaction vessel. The contents of the reaction vessel were maintained at 40 °C and the pCl was 1.95.

While this solution was vigorously stirred, 30 mL of 1.0 M silver nitrate solution and 30 mL of a 0.99 M sodium chloride and 0.01 M potassium iodide solution were added simultaneously at a rate of 30 mL/min each. This achieved grain nucleation to form crystals with an initial iodide concentration of 2 mole percent, based on total silver.

The mixture was then held 10 minutes with the temperature remaining at 40 °C. Following the hold, a 1.0 M silver nitrate solution and a 1.0 M NaCl solution were then added simultaneously at 2 mL/min for 40 minutes with the pCl being maintained at 1.95.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 0.5 mole percent iodide, based on silver. Fifty percent of total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.84 μm and an average thickness of 0.037 μm, selected on the basis of an aspect ratio rank ordering of all {100} tabular grains having a thickness of less than 0.3 μm and a major face edge length ratio of less than 10. The selected tabular grain population had an average aspect ratio (ECD/t) of 23 and an average tabularity (ECD/t^2) of 657. The ratio of major face edge lengths of the selected tabular grains was 1.4. Seventy two percent of total grain projected area was made up of tabular grains having {100} major faces and aspect ratios of at least 7.5. These tabular grains had a mean ECD of 0.75 μm, a mean thickness of 0.045 μm, a mean aspect ratio of 18.6 and a mean tabularity of 488.

A representative sample of the grains of the emulsion is shown in Figure 1.

Emulsion Preparation Example 2 (Comparative)

This emulsion demonstrates the importance of iodide in the precipitation of the initial grain population (nucleation).

This emulsion was precipitated identically to that of Example 1, except no iodide was intentionally added.

The resulting emulsion consisted primarily of cubes and very low aspect ratio rectangular grains ranging in size from about 0.1 to 0.5 μm in edge length. A small number of large rods and high aspect ratio {100} tabular grains were present, but did not constitute a useful quantity of the grain population.

A representative sample of the grains of this emulsion is shown in Figure 2.

Example 3

Emulsion Precipitations

Emulsion A: silver chloride cubic emulsion

A monodisperse silver chloride cube with a cubic edge length of 0.59 μm was prepared by simultaneous addition of 3.75 M silver nitrate and 3.75 M sodium chloride to a well stirred solution containing 8.2 g/l of sodium chloride, 28.2 g/l of bone gelatin and 0.212 g/liter of 1,8-dithiadioctanediol while maintaining the temperature at 68.3 °C and the pCl at 1.0. The temperature was reduced to 40 ° C and the emulsion was washed by ultrafiltration to a pCl of 2.0, then adjusted to a pCl of 1.65 with sodium chloride.

Emulsion B: (100) surface high chloride tabular emulsion

A 1.5 L solution containing 3.52% by weight of low methionine gelatin, 0.0056 M sodium chloride and 0.3 ml of polyethylene glycol antifoamant was provided in a stirred reaction vessel at 40 ° C. While the solution was vigorously stirred, 45 ml of a 0.01 M potassium iodide solution was added followed by 50 mL of 1.25 M silver nitrate and 50 mL of a 1.25 M sodium chloride solution added simultaneously at a rate of 100 mL/min each. The mixture was then held for 10 seconds with the temperature remaining at 40 ° C. Following the hold, a 0.625 M silver nitrate solution containing 0.08 mg mercuric chloride per mole of silver nitrate and a 0.621 M sodium chloride and 0.004 M potassium iodide solution were added simultaneously at 10 mL/min for 30 minutes followed by a linear acceleration from 10 mL/min to 15 mL/min over 125 minutes. This was followed by constant flow rate growth for 30 minutes at 15 mL/min while maintaining the pCl at 1.8. The pCl was then adjusted to 1.65 with sodium chloride. 50 g of phthalated gelatin was added and the emulsion was washed and concentrated. The pCl after washing was 2.0. 21 g of low methionine gel was added and the pCl was adjusted to 1.65 with sodium chloride and the pH was adjusted to 5.7. The resulting

emulsion was a tabular grain silver chloride emulsion containing 0.036 mole percent iodide with a mean equivalent circular grain diameter of 1.6 and a mean grain thickness of 0.125 μm.

Sensitization

Emulsion A:

An optimum green light sensitization was found by varying the level of sensitizing dye, sensitizing agents and digestion time. The conditions for the optimum were as follows: to a 0.05 mole quantity of Emulsion A melted at 40 ° C and well stirred, were added the following; 600 mg/mole of potassium bromide, followed by 0.214 mmol/mole of sensitizing dye A, then a 20 minute hold, then 0.036 mmol/mole of sensitizing dye B followed by another 20 minute hold. To this was added 0.75 mg/mol of sodium thiosulfate pentahydrate and 1.0 mg/mole of potassium tetrachloroaurate. The temperature was then increased to 60 °C over 6 minutes, held for 10 minutes then ramped to 40 °C over 18 minutes. 70 mg/mole of 1-(3-acetamidophenyl)-5-mercaptotetrazole was then added and the emulsion was chill set.

Emulsion B:

An optimum green light sensitization was found in a similar manner to Emulsion A. The optimum condition were as follows: To a suitable quantity of well stirred emulsion at 40 °C, 0.80 mmole of sensitizing dye A was added, followed by a 20 minute hold. To this was added 3.0 mg/mole of sodium thiosulfate pentahydrate and 1.5 mg/mole of potassium tetrachloroaurate. The temperature was then increased to 60 °C over 6 minutes, held for 20 minutes then ramped to 40 °C over 18 minutes. 70 mg/mole of 1-(3-acetamidophenyl)-5-mercaptotetrazole was then added and the emulsion was chill set.

Photographic Coatings

Each of the sensitized emulsions was coated on an antihalation support at 0.85 g/m^2 of silver along with 1.1 g/m^2 of cyan dye forming coupler A, 2.7 g/m^2 of gelatin and varying amounts (shown in Table 1) of development inhibitor releasing coupler B. These were overcoated with 1.6 g/m^2 of gelatin and hardened with bis(vinyl-sulfonylmethyl)ether.

Exposure

Sensitivity to green light was measured by exposing the coatings for 0.01 seconds using a step wedge sensitometer with a 3000K tungsten lamp filtered to simulate a Daylight source and filtered to transmit only green and red light by a Kodak Wratten 9 filter.

Process

The coatings were processed as shown below using either Developer A or B. The photographic response was evaluated for development times of 30, 60 and 120 seconds.

Process Solutions and Process Sequences Process

Develop	See Table 1	38 °C
Bleach	240"	38 °C
Wash	180"	35 °C
Fix	240"	38 °C
Wash	180"	35 °C
Rinse	60"	35 °C

The process solution compositions are as follows:

	Tank	
Developer-A		
Water	800.0	mL
Potassium Carbonate, anhydrous	34.30	g
Potassium bicarbonate	2.32	g
Sodium sulfite, anhydrous	0.38	g
Sodium metabisulfite	2.96	g
Potassium Iodide	1.20	mg
Sodium Bromide	1.31	g
4-methoxyphenidone	0.20	g

Diethylenetriamine pentaacetic acid pentasodium salt (40% solution)	8.43	g
Hydroxylamine sulfate	2.41	g
(N-(4-amino-3-methylphenyl)-N-ethyl-2-aminoethanol)	4.52	g
Water to make pH @ 80F 10.00 +/- 0.05	1.0	L

Developer-B

Water	800.0	mL
Potassium Carbonate, anhydrous	34.30	g
Potassium bicarbonate	2.32	g
Sodium sulfite, anhydrous	0.38	g
Sodium metabisulfite	2.96	g
Potassium Iodide	1.20	mg
Sodium Bromide	1.31	g
Diethylenetriaminepentaacetic acid pentasodium salt (40% solution)	8.43	g
Hydroxylamine sulfate	2.41	g
(N-(4-amino-3-methylphenyl)-N-ethyl-2-aminoethanol)	4.52	g
Water to make pH @ 80F 10.00 +/- 0.05	1.0	L

Bleach

Water	500.0	mL
1,3-propylenediamine tetraacetic acid	37.4	g
57% ammonium hydroxide	70.0	mL
Acetic acid	80.0	mL
2-hydroxy-1,3-propylenediamine tetraacetic acid	0.80	g
Ammonium Bromide	25.0	g
Ferric nitrate nonahydrate	44.85	g
Water to make pH 4.75	1.0	L

Fix		
Water	500.0	mL
Ammonium Thiosulfate (58% solution)	214.0	g
(Ethylenedinitrilo)tetraacetic acid disodium salt, dihydrate	1.29	g
Sodium metabisulfite	11.0	g
Sodium Hydroxide (50% solution)	4.70	g
Water to make pH at 80F 6.5 +/- 0.15	1.0	L
Rinse		
Water	900.0	mL
0.5% Aqueous p-tertiary-octyl-(alpha-phenoxypolyethyl)-alcohol	3.0	mL
Water to make	1.0	L

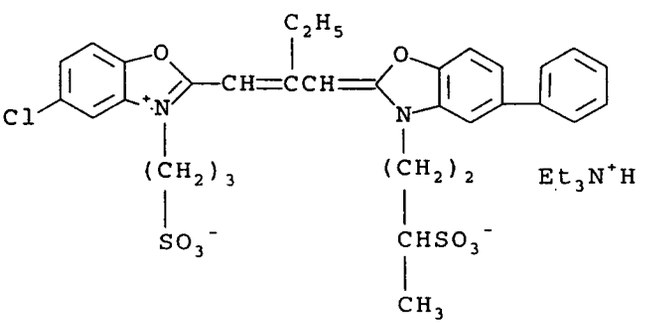
The results are shown in Table 1 below.

TABLE 1

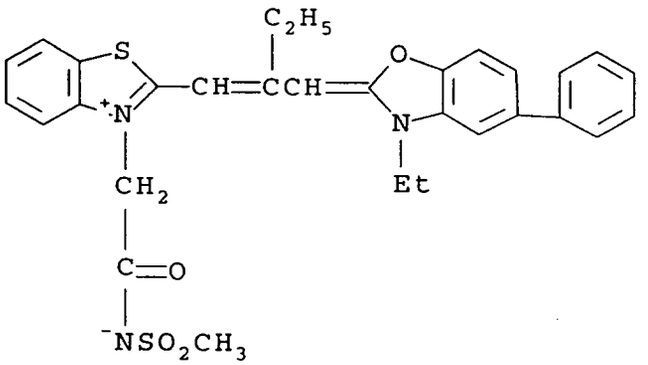
DIR coupler level g/m^2	development time seconds	relative speed		gamma		minimum density	
		dev A (inv.)	dev B (comp.)	dev A (inv.)	dev B (comp.)	dev A (inv.)	dev B (comp.)
Emulsion A (cube):							
0	30	132	100	1.62	1.72	0.05	0.06
0	60	144	132	2.65	2.37	0.05	0.06
0	120	155	150	4.06	3.05	0.07	0.07
1.9E-4	30	143	108	1.00	0.95	0.05	0.06
1.9E-4	60	141	135	2.39	2.04	0.05	0.06
1.9E-4	120	157	153	2.46	2.28	0.07	0.07
3.8E-4	30	149	119	0.74	0.65	0.05	0.06
3.8E-4	60	140	143	2.22	1.23	0.05	0.06
3.8E-4	120	156	153	2.36	2.29	0.07	0.07
Emulsion B (tabular):							
0	30	207	153	1.14	1.31	0.09	0.08
0	60	233	210	1.91	1.75	0.13	0.14
0	120	255	241	2.09	2.20	0.33	0.27
1.9E-4	30	215	152	1.06	1.19	0.10	0.08
1.9E-4	60	241	208	1.28	1.39	0.15	0.14
1.9E-4	120	254	243	1.69	1.60	0.33	0.28
3.8E-4	30	227	167	0.80	0.78	0.09	0.07
3.8E-4	60	240	215	1.45	1.19	0.14	0.13
3.8E-4	120	261	245	1.38	1.33	0.32	0.25

Table 1 shows that the speeds for both emulsions when developed for 30 seconds in developer A are equal to or greater than the speeds when developed for 60 seconds in developer B, while the gamma for the 30 second developer A process was significantly lower than the gamma for the 60 second developer B process. The Dmin does not change significantly. This shows that the inventive combination produces equivalent speeds to the conventional process at lower gamma and at much shorter development times. Also the speeds of Emulsion B, even at the shortest development times are much greater than any speed attained by Emulsion A. This shows that the combination of a high chloride tabular emulsion with the latent image detection enhanced developer produces the highest speeds at low gamma and short development times.

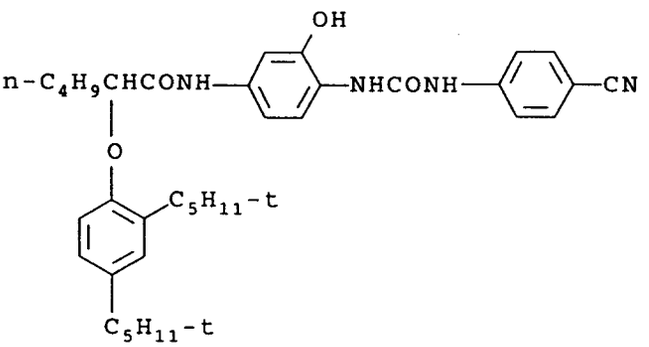
Sensitizing Dye A



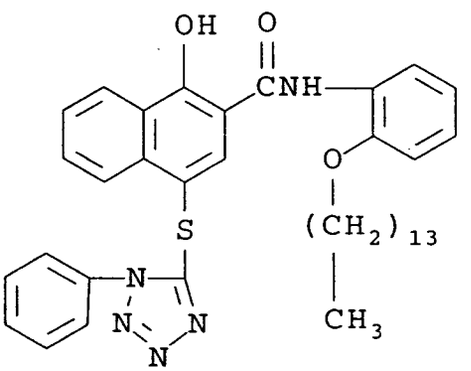
Sensitizing Dye B)



Coupler A



Coupler B



Example 4 - Preparation and Processing of an Element Containing an Electron Transfer Agent-Releasing Compound

A. Preparation of Elements

Samples 514 and 515 were prepared by applying the following layers to a clear support in the order indicated. Quantities of components are expressed in grams per square meter.

Layer 1 (antihalation layer) comprising gray silver and gelatin.

Layer 2 (light sensitive layer) comprising 0.538 g of a tabular AgCl emulsion with an average ECD of 1.4 μm and an average thickness of 0.14 μm, tabular grains bounded by {100} faces accounted for greater than 50% of the projected grain area; 1.82 g gelatin; image dye forming coupler C-31 at 0.646 g; DIR compound D-3 at 0.054 g; and compound B-1 at 0.054 g; and, in sample 515, the electron transfer agent-releasing (ETAR) compound C-52 at 0.032 g.

Layer 3 (protective layer) comprising 2.15 g of gelatin.

The layers additionally comprised alpha-4-nonylphenyl-omega-hydroxy-poly(oxy-(2-hydroxy-1,3-propanediyl)) and (para-t-octylphenyl)-di(oxy-1,2-ethanediyl)-sulfonate as surfactants.

These films were hardened at coating with 2% by weight to total gelatin of bis-vinylsulfonylmethane.

B. Effect of an electron transfer agent-releasing (ETAR) compound on sensitivity, gamma, and density of an element

Samples 514 and 515 were exposed to white light through a graduated density test object and processed using the KODAK® C-41 process. The bleach used in the process was modified to comprise 1,3-propylenediamine-tetraacetic acid. The relative sensitivities, gammas, and maximum densities of the processed elements were determined. These values are reported in Table 2.

Table 2

Effect on photographic sensitivity, gamma and density formation produced by electron transfer agent releasing (ETAR) compound.					
Sample	Image-Forming Coupler	ETAR Compound (quantity)	Sensitivity	Relative Gamma	Density
514	C-31	none	100.0%	100.0%	100.0%
515	C-31	C-52 (0.032)	407.4%	115.1%	113.8%

As can be seen, the ETAR compound improved the sensitivity, density, and gamma of the element of the invention containing it. As illustrated in this example, ETAR compounds can also be used in combination with other PUG-releasing compounds described elsewhere herein.

Claims

1. A method of processing an exposed originating silver halide color photographic element comprising developing the photographic element in a color devoloper solution containing a p-phenylenediamine color developing agent in the presence of a 1-phenyl pyrazolidin-3-one compound;

wherein the originating silver halide photographic element comprises a radiation sensitive emulsion in reactive association with a development inhibitor releasing compound and containing a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population projected area, wherein at least 50 percent of total grain projected area is accounted for by intrinsically stable tabular grains

(1) bounded by {100} major faces having adjacent edge ratios of less than 10 and

(2) each having an aspect ratio of at least 2, and wherein the silver halide content of the photographic element comprises at least 50 mole % silver chloride and no more than 2 mole % silver iodide.

2. The method of claim 1 wherein the tabular silver halide grains have an aspect ratio of at least 8.

3. The method of claim 1 or claim 2 wherein the tabular silver halide grains have thicknesses of less than 0.3 microns.

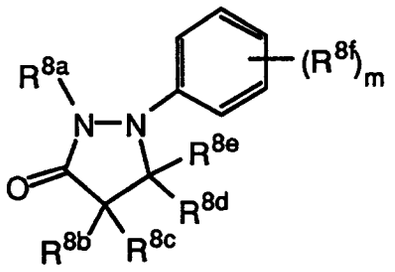
4. The method of any one of the preceding claims wherein the tabular silver halide grains contain at least 70 mole percent chloride.

5. The method of any one of the preceding claims wherein the 1-phenyl pyrazolidin-3-one compound is contained in the originating silver halide photographic element in an inactive form from which the active form is released during processing.

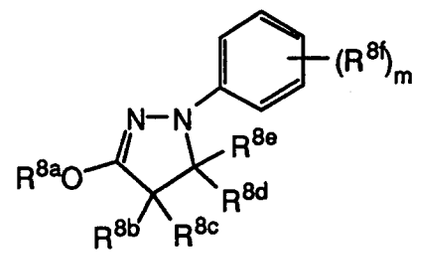
6. The method of any one of claims 1 to 4 wherein the 1-phenyl pyrazolidin-3-one compound is contained in the color developer solution.

7. The method of any one of claims 1 to 4 wherein the 1-phenyl pyrazolidin-3-one compound is represented by Formula I or II

Formula I



Formula II



wherein:

R^{8a} is hydrogen;

R^{8b} and R^{8c} each independently represent a hydrogen, a substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms or a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms;

R^{8d} and R^{8e} each independently represent a hydrogen, a substituted or unsubstituted alkyl group having from 1 to 10 carbon atoms or a substituted or unsubstituted aryl group having from 6 to 10 carbon atoms;

unsubstituted aryl group having from 6 to 10 carbon atoms;

R^{8f} is independently a hydrogen, a halogen, a substituted or unsubstituted alkyl group having from 1 to 8 carbon atoms, or a substituted or unsubstituted alkoxy group having from 1 to 8 carbon atoms, or a sulfonamido group, and when m is greater than 1, the R^{8f} substituents can be taken together to form a carbocyclic or a heterocyclic ring; and

m is 1 to 3.

8. The method of claim 7 wherein

m is 2;

the R^{8f} substituents are in the para and meta positions of the benzene ring and each is a hydrogen or an alkoxy group having 1-4 carbon atoms, and

R^{8b} and R^{8c} are each hydrogen or an alkyl group having 1-10 carbon atoms, providing that one of R^{8f} isan alkoxy group or one of R^{8b} and R^{8C} is an alkyl group of 3-7 carbon atoms.

9. The method of claim 8 wherein at least one R^{8f} is an alkoxy group of 1-4 carbon atoms, R^{8b} is hydrogen or an alkyl group of 1-4 carbon atoms, and R^{8c} is hydrogen or a hydroxyalkyl group of 1-4 carbon atoms.

10. The method of claim 9 wherein the 1-phenyl pyrazolidin-3-one compound is 1-(4-methoxyphenyl)-3-pyrazolidone.

FIG 1

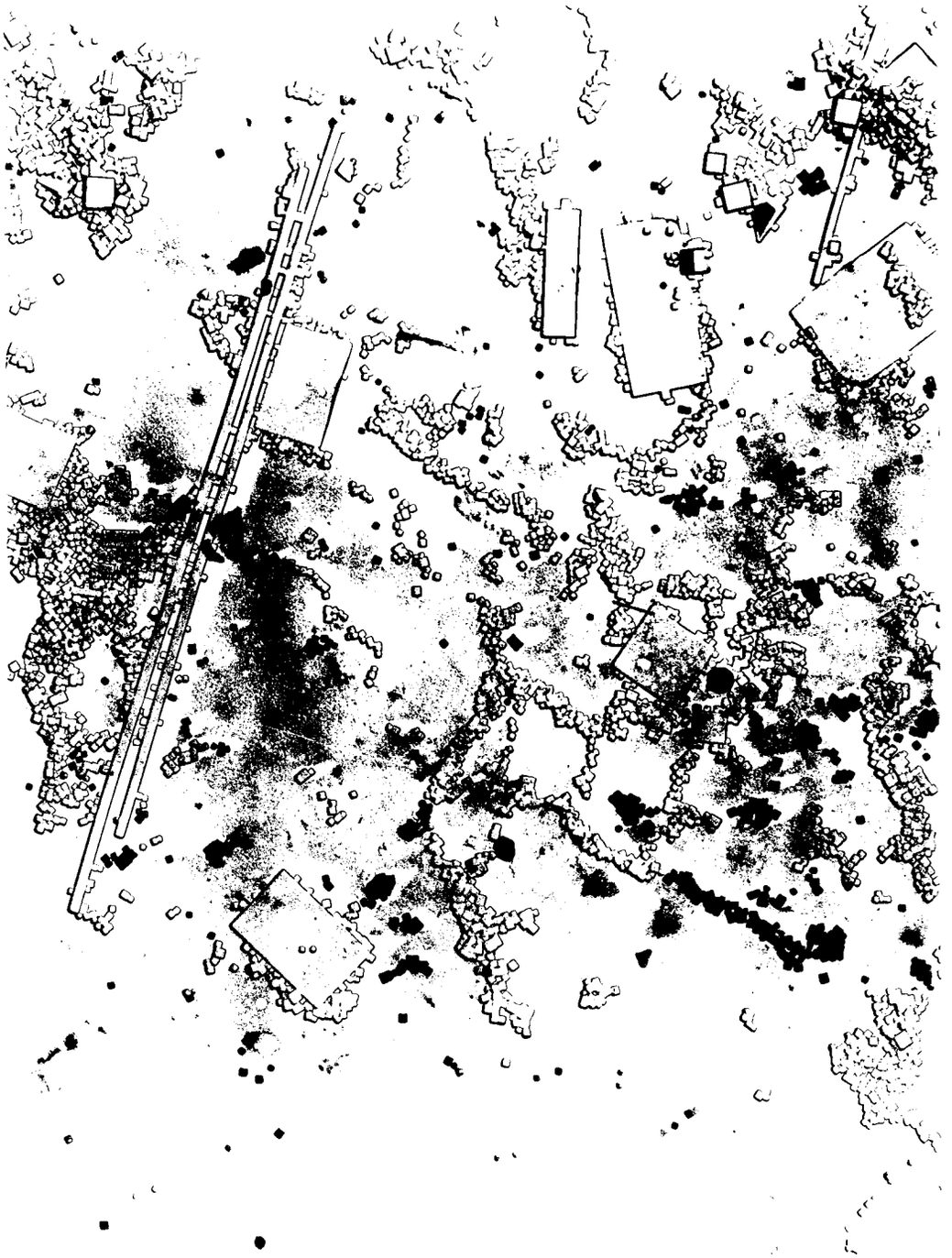


FIG. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 20 0681

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	US-A-4 845 016 (ISHIKAWA ET AL.) * column 2, line 46 - column 3, line 2 * * column 3, line 26 - column 11, line 10 * * column 13, line 8 - line 29 * * column 43, line 38 - line 42 * * column 44, line 13 - line 19 * * column 46, line 16 - line 21 *	1-10	G03C1/005 G03C7/392 G03C7/413
Y	FR-A-2 295 454 (CIBA-GEIGY) * page 4, line 8 - line 13 * * page 4, line 21 - line 25; claim 1 *	1-10	
Y	WO-A-92 10789 (KODAK) * page 6, line 14 - line 16 * * page 7, line 4 - line 6; claims 1-12 *	1-10	
P,A	EP-A-0 534 395 (KODAK) * page 19, line 55 - line 56; claims 1-9 *	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 May 1994	Magrizos, S

CATEGORY OF CITED DOCUMENTS

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

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)