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

(11) Publication number: **0 617 320 A2**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **94104414.1**

(22) Date of filing: **21.03.94**

(51) Int. Cl.^{5}: **G03C 1/005**, G03C 1/34

(30) Priority: **22.03.93 US 34317**

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

(84) Designated Contracting States:
BE CH DE FR GB IT LI NL

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

(72) Inventor: **Lok, Roger, Eastman Kodak Company**
Patent Legal Staff,
343 State Street
Rochester, New York 14650-2201 (US)
Inventor: **Budz, Jerzy Antoni, Eastman Kodak Company**
Patent Legal Staff,
343 State Street
Rochester, New York 14650-2201 (US)

(74) Representative: **Brandes, Jürgen, Dr. rer. nat. et al**
Wuesthoff & Wuesthoff
Patent- und Rechtsanwälte
Schweigerstrasse 2
D-81541 München (DE)

(54) Tabular grain emulsions containing antifoggants and stabilizers.

(57) A radiation sensitive emulsion stabilized against changes in sensitivity and fog upon aging is disclosed. The radiation sensitive emulsion contains a silver halide grain population comprising at least 50 mole percent chloride, based on silver, wherein at least 50 percent of the grain population projected area is accounted for by tabular grains (a) bounded by {100} major faces having adjacent edge ratios of less than 10, and (b) each having an aspect ratio of at least 2. The emulsion contains a stabilizer which is (A) a mercapto heterocyclic nitrogen compound containing a mercapto group bonded to a carbon atom which is linked to an adjacent nitrogen atom in a heterocyclic ring system, (B) a quaternary aromatic chalcogenazolium salt wherein the chalcogen is sulfur, selenium or tellurium, (C) a triazole or tetrazole containing an ionizable hydrogen bonded to a nitrogen atom in a heterocyclic ring system, (D) a dichalcogenide compound comprising an -X-X- linkage between carbon atoms wherein each X is divalent sulfur, selenium or tellurium, (E) an organic compound containing a thiosulfonyl group having the formula $-SO_2SM$ where M is a proton or cation, (F) a mercuric salt, or (G) a quinone compound. Photographic elements, particularly color photographic elements containing this emulsion are also disclosed.

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(3.10/3.09/3.3.4)

FIG. 1

The invention relates to a radiation sensitive tabular grain silver halide emulsion with enhanced sensitivity and improved storage properties.

Silver halide emulsions having high chloride contents, e.g., greater than 50 mole percent chloride based on silver, are known to be very desirable in image-forming systems due to the high solubility of silver chloride, which permits short processing times and provides less environmentally polluting effluents. Unfortunately, the higher the chloride content of a silver halide emulsion, the more difficult it is to achieve high and stable radiation sensitivity (sometimes referred to in the photographic art as "speed"). One reason for this is that conventional emulsions having high chloride contents exhibit a severe propensity to deterioration upon aging or storage. As a consequence, such an aged or stored emulsion when processed, produces a higher minimum density than the "fresh" emulsion. This increase in minimum density, commonly referred to as "fog", is attributable to the formation of a low level of reduced silver formation that occurs independently of imagewise exposure. In color photography, fog is typically observed as image dye density, rather than directly as silver density. Changes in fog and sensitivity are particularly troublesome in color photographic elements that comprise multiple color layers since such changes can vary from layer to layer which results in a color imbalance and reduction in quality.

Materials known in the photographic art as photographic "stabilizers", as distinguished from the general class of "antifoggants", have been used in the past to protect radiation sensitive silver halide emulsions against changes in sensitivity and fog upon aging and storage. One skilled in the art readily recognizes the distinction between the use of photographic stabilizers, which combat fog and sensitivity changes that occur upon storage, and those materials, categorized as antifoggants, which combat fog caused by such things as the inherent nature of the radiation sensitive silver halide emulsion (which may produce chemical fog) or the conditions of development of the emulsion, for example, development for protracted periods of time or at temperatures above normal. A more detailed discussion of this distinction between antifoggants and stabilizers can be found in G.F. Duffin, *Photographic Emulsion Chemistry*, Chapter 7, The Focal Press, London and New York (1966), *Research Disclosure*, August 1976, Item 14851 and U.S. Patent No. 2,728,663.

An extensive description of photographic stabilizers and antifoggants which are indicated to be useful for avoiding instability that increases minimum density in negative-type emulsion coatings (i.e., fog) or that increases minimum density or decreases maximum density in direct-positive emulsion coatings is set forth in *Research Disclosure*, Vol. 308, December 1989, Item 308119, Section VI. *Research Disclosure* is published by Kenneth Mason Publication, Ltd., the Old Harbourmaster's, 8 North Street, Emsworth, Hampshire PO10 7DD, England. In addition, Nishikawa et al., U.S. Patent No. 4,960,689, describes a color photographic material that comprises a silver halide emulsion containing at least 50 mole percent chloride and a compound that is referred to as an antifoggant. Also, Japanese published Patent Application (Kokai) 03/208,041, laid open September 11, 1991, describes a silver halide color photographic material having a silver halide emulsion layer in which the emulsion is prepared in the presence of a thiosulfonate compound.

It is known that certain tabular grain silver halide emulsions can offer a number of photographic advantages. Thus, during the 1980's a marked advance took place in silver halide photography based on the discovery that a wide range of photographic advantages, such as improved speed-granularity relationships, increased covering power both on an absolute basis and as a function of binder hardening, more rapid developability, increased thermal stability, increased separation of native and spectral sensitization imparted imaging speeds and improved image sharpness in both mono- and multi-emulsion layer formats, could be achieved by employing tabular grain emulsions.

An emulsion is generally understood to be a "tabular grain emulsion" when tabular grains account for at least 50 percent of the grain population projected area. A grain is generally considered to be a tabular grain when the ratio of its equivalent circular diameter (ECD) to its thickness (t) is at least 2. The equivalent circular diameter of a grain is the diameter of a circle having an area equal to the projected area of the grain. The term "intermediate aspect ratio tabular grain emulsion" refers to an emulsion which has an average tabular grain aspect ratio in the range of from 5 to 8. The term "high aspect ratio tabular grain emulsion" refers to an emulsion which has an average tabular grain aspect ratio of greater than 8. The term "thin tabular grain" is generally understood to be a tabular grain having a thickness of less than 0.2 μm. The term "ultrathin tabular grain" is generally understood to be a tabular grain having a thickness of 0.06 μm or less. The term "high chloride" refers to grains that contain at least 50 mole percent chloride based on silver. In referring to grains of mixed halide content, the halides are named in order of increasing molar concentrations--e.g., silver iodochloride contains a higher molar concentration of chloride than iodide.

The overwhelming majority of known tabular grain emulsions contain tabular grains that are irregular octahedral grains. Regular octahedral grains contain eight identical crystal faces, each lying in a different {111} crystallographic plane. Tabular irregular octahedra contain two or more parallel twin planes that separate two major grain faces lying in {111} crystallographic planes. The {111} major faces of the tabular grains exhibit a threefold symmetry, appearing triangular or hexagonal. It is generally accepted that the tabular shape of the grains is the result of the twin planes producing favored edge sites for silver halide deposition, with the result that the grains grow laterally while increasing little, if any, in thickness after parallel twin plane incorporation.

While tabular grain emulsions have been advantageously employed in a wide variety of photographic and radiographic applications, the requirement of parallel twin plane formation and {111} crystal faces pose limitations both in emulsion preparation and use. These disadvantages are most in evidence in considering tabular grains containing significant chloride concentrations. It is generally recognized that silver chloride grains prefer to form regular cubic grains--that is, grains bounded by six identical {100} crystal faces. Tabular grains bounded by {111} faces in silver chloride emulsions often revert to nontabular forms unless morphologically stabilized.

While tabular grain silver bromide emulsions were known to the art long before the 1980's, Wey U.S. Patent 4,399,215 produced the first tabular grain silver chloride emulsion. The tabular grains were of the twinned type, exhibiting major faces of threefold symmetry lying in {111} crystallographic planes. An ammoniacal double-jet precipitation technique was employed. The thicknesses of the tabular grains were high compared to contemporaneous silver bromide and bromoiodide tabular grain emulsions because the ammonia ripening agent thickened the tabular grains. To achieve ammonia ripening it was also necessary to precipitate the emulsions at a relatively high pH, which is known to produce elevated minimum densities (fog) in high chloride emulsions. Further, to avoid degrading the tabular grain geometries sought both bromide and iodide ions were excluded from the tabular grains early in their formation.

Wey et al U.S. Patent 4,414,306 developed a twinning process for preparing silver chlorobromide emulsions containing up to 40 mole percent chloride based on total silver. This process of preparation has not been successfully extended to high chloride emulsions. The highest average aspect ratio reported in the Examples was 11.

Maskasky U.S. Patent 4,400,463 (hereinafter designated Maskasky I) developed a strategy for preparing a high chloride emulsion containing tabular grains with parallel twin planes and {111} major crystal faces with the significant advantage of tolerating significant internal inclusions of the other halides. The strategy was to use a particularly selected synthetic polymeric peptizer in combination with a grain growth modifier having as its function to promote the formation of {111} crystal faces. Adsorbed aminoazaindenes, preferably adenine, and iodide ions were disclosed to be useful grain growth modifiers.

Maskasky U.S. Patent 4,713,323 (hereinafter designated Maskasky II), significantly advanced the state of the art by preparing high chloride emulsions containing tabular grains with parallel twin planes and {111} major crystal faces using an aminoazaindene growth modifier and a gelatino-peptizer containing up to 30 micromoles per gram of methionine. Since the methionine content of a gelatino-peptizer, if objectionably high, can be readily reduced by treatment with a strong oxidizing agent (or alkylating agent, King et al U.S. Patent 4,942,120), Maskasky II placed within reach of the art high chloride tabular grain emulsions with significant bromide and iodide ion inclusions prepared starting with conventional and universally available peptizers.

Maskasky I and II have stimulated further investigations of grain growth modifiers capable of preparing high chloride emulsions of similar tabular grain content. Tufano et al U.S. Patent 4,804,621 employed di-(hydroamino)azines as grain growth modifiers; Takada et al U.S. Patent 4,783,398 employed heterocycles containing a divalent sulfur ring atom; Nishikawa et al U.S. Patent 4,952,491 employed spectral sensitizing dyes and divalent sulfur atom containing heterocycles and acyclic compounds; and Ishiguro et al U.S. Patent 4,983,508 employed organic bis-quaternary amine salts.

Bogg U.S. Patent 4,063,951 reported the first tabular grain emulsions in which the tabular grains had parallel {100} major crystal faces. The tabular grains of Bogg exhibited square or rectangular major faces, thus lacking the threefold symmetry of conventional tabular grain {111} major crystal faces. In the sole example Bogg employed an ammoniacal ripening process for preparing silver bromoiodide tabular grains having aspect ratios ranging from 4:1 to 1:1. The average aspect ratio of the emulsion was reported to be 2, with the highest aspect ratio grain (grain A in Figure 3) being only 4. Bogg states that the emulsions can contain no more than 1 percent iodide and demonstrates only a 99.5% bromide 0.5% iodide emulsion. Attempts to prepare tabular grain emulsions by the procedures of Bogg have been unsuccessful.

In light of the previous discussion, it is evident that the problem of this invention is to provide a high chloride tabular grain silver halide emulsion which is (1) inherently physically stable in a tabular form even in the absence of an adsorbed species to provide morphological stability and (2) protected against deleterious changes in fog and sensitivity upon aging (sometimes referred to in the art as improved keeping). The radiation sensitive high chloride tabular grain emulsion of this invention, as described and claimed hereinafter, provides a solution to this problem.

In accordance with this invention, we have found that certain novel tabular grain silver halide emulsions containing tabular grains having a high chloride content and bounded by {100} major faces which meet specific criteria and contain photographic stabilizers, as described in greater detail hereinafter, exhibit excellent storage properties. In one aspect the invention is directed to a radiation sensitive emulsion containing a silver halide grain population comprising at least 50 mole percent chloride, based on silver, wherein at least 50 percent of the grain population projected area is accounted for by tabular grains (a) bounded by {100} major faces having adjacent edge ratios of less than 10, and (b) each having an aspect ratio of at least 2. The emulsion comprises a photographic stabilizer that protects it against changes in fog and sensitivity upon aging. The stabilizer is a compound that is (A) a mercapto heterocyclic nitrogen compound containing a mercapto group bonded to a carbon atom which is linked to an adjacent nitrogen atom in a heterocyclic ring system, (B) a quaternary aromatic chalcogenazolium salt wherein the chalcogen is sulfur, selenium or tellurium, (C) a triazole or tetrazole containing an ionizable hydrogen bonded to a nitrogen atom in a heterocyclic ring system, (D) a dichalcogenide compound comprising an -X-X- linkage between carbon atoms wherein each X is divalent sulfur, selenium or tellurium, (E) an organic compound containing a thiosulfonyl group having the formula $-SO_2SM$ where M is a proton or cation, (F) a mercuric salt, or (G) a quinone compound.

In another aspect, this invention is directed to a photographic element, particularly a color photographic element, having a support bearing at least one layer comprising the radiation sensitive tabular grain emulsion described in the preceding paragraph.

As illustrated by the following Examples, the tabular grain silver halide emulsions of this invention (sometimes referred to herein simply as high chloride {100} tabular grain emulsions) are protected against excessive deleterious changes in sensitivity and fog upon aging by the stabilizers listed, which are sometimes referred to hereinafter simply by group, e.g. Group A-G photographic stabilizers. Furthermore, photographic elements containing high chloride {100} tabular grain emulsions of the type described herein retain the advantages of faster and easier processability and provide less environmentally polluting effluents which is an additional significant advantage of this invention.

The present invention has been facilitated by the discovery of a novel approach to forming tabular grains. Instead of introducing parallel twin planes in grains as they are being formed to induce tabularity and thereby produce tabular grains with {111} major faces, it has been discovered that the presence of iodide in the dispersing medium during a high chloride nucleation step coupled with maintaining the chloride ion in solution within a selected pCl range results in the formation of a tabular grain emulsion in which the tabular grains are bounded by {100} crystal faces.

The above approach to forming tabular grains places within the reach of the art tabular grains bounded by {100} crystal faces with grain compositions and grain thicknesses that have not been heretofore realized. For example, one can obtain an ultrathin tabular grain emulsion in which the grains are bounded by {100} crystal faces. In a preferred form the process described herein provides intermediate and high aspect ratio tabular grain high chloride emulsions exhibiting high levels of grain stability. Unlike high chloride tabular grain emulsions in which the tabular grains have {111} major faces, such emulsions do not require a morphological stabilizer adsorbed to the major faces of the grains to maintain their tabular form. Finally, while clearly applicable to high chloride emulsions containing iodide, the process described herein also extends to silver chloride and silver bromochloride emulsions, each of which can be prepared by variant precipitation procedures that do not require the presence of iodide ion during grain nucleation.

Brief Description of the Drawings

Figure 1 is a shadowed photomicrograph of carbon grain replicas of an emulsion prepared as described in Example 1, which is a representative emulsion of this invention.

Figure 2 is a shadowed photomicrograph of carbon grain replicas of a control emulsion prepared as described in Example 1.

The identification of tabular grain silver halide emulsions satisfying the requirements necessary for this invention can be better appreciated by considering a representative tabular grain emulsion. Figure 1 is a shadowed photomicrograph of carbon grain replicas of such an emulsion, prepared as described in Example 1 which follows. It is immediately apparent from Figure 1 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 the grain population 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 the grain population projected area. From the preceding definition of a tabular grain, it is apparent that the average aspect ratio of the tabular grains can only approach 2 a minimum limit. In fact, the tabular grain emulsions of this invention typically exhibit average aspect ratios of 5 or more, with high average aspect ratios (greater than 8) being preferred. That is, preferred emulsions of the invention are high aspect ratio tabular grain emulsions. In specifically preferred emulsions, 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 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 hereinbefore. 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 the grain population 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 benefits that can be gained 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 m 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.

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 grain population projected area is provided by tabular grains also exhibiting a thickness of less than 0.2 μm. In other words, the emulsions are in this instance thin tabular grain emulsions.

Surprisingly, ultrathin tabular grain emulsions have been prepared which satisfy the requirements needed in the recording elements used in 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 preparation technique 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 prepared as described herein 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 described herein 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 grain population 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 our invention.

The tabular grain population can exhibit an average ECD of any 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 herein accounts for at least 50 percent of the grain population projected area a 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 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 described herein 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 the grain population projected area.

So long as tabular grains having the desired characteristics described herein account for the requisite proportion of the grain population projected area, the remainder of the grain population 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 required tabular grain descriptions are specifically contemplated.

If tabular grains satisfying the tabular grain population requirements do not account for 50 percent of the grain population projected area, the emulsion does not satisfy the requirements for 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 for the invention have an excessive proportion of grain population projected area accounted for by cubes, twinned nontabular grains, and rods. Such an emulsion is shown in Figure 2 (Example 1 control emulsion). 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 grain population projected area.

The tabular grain emulsion of Figure 1 satisfying the requirements for 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 for 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 growth accelerating irregularities in one or more of the cubic crystal faces. The cubic crystal faces that contain at least one irregularity thereafter accept silver halide at an accelerated rate as compared to the regular cubic crystal faces (i.e., those lacking an irregularity). When only one of the cubic crystal faces contains an irregularity, grain growth on only one face is accelerated, and the resulting grain structure on continued growth is a rod. The same result occurs when only two opposite parallel faces of the cubic crystal structure contain irregularities. However, when any two contiguous cubic crystal faces contain an irregularity, continued growth accelerates growth on both faces and produces a tabular grain structure. It is believed that the tabular grains of the emulsions of this invention are produced by those grain nuclei having two, three or four faces containing growth accelerating irregularities.

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

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 hereinbefore as the nucleation step is in reality a step for introduction of grain facet irregularities. The disadvantage of delaying the introduction of grain facet irregularities is that this produces thicker tabular grains than would otherwise be obtained.

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

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 herein for use in the invention.

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

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

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

If desired, the rate of ripening can be increased by the presence of a ripening agent in the emulsion during the holding period. A conventional simple approach to accelerating ripening is to increase the halide ion concentration in the dispersing medium. This creates complexes of silver ions with plural halide ions that accelerate ripening. When this approach is employed, it is preferred to increase the chloride ion concentration in the dispersing medium. That is, it is preferred to lower the pCl of the dispersing medium into a range in which increased silver chloride solubility is observed. Alternatively, ripening can be accelerated and the percentage of the grain population projected area accounted for by {100} tabular grains can be increased by employing conventional ripening agents. Preferred ripening agents are sulfur containing ripening agents, such as thioethers 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 the grain population projected accounted by the {100} tabular grains.

Once the desired population of grain nuclei have been formed, grain growth can proceed according to any convenient conventional precipitation technique for the precipitation of silver halide grains bounded by {100} grain faces. Whereas iodide and chloride ions are required to be incorporated into the grains during nucleation and are therefore present in the completed grains at the internal nucleation site, any halide or combination of halides known to form a cubic crystal lattice structure can be employed during the growth step. Neither iodide nor 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 grain preparation the nucleation and growth stages of grain precipitation occur in the same reaction vessel. It is, however, recognized that grain precipitation can be interrupted, particularly after completion of the nucleation stage. Further, two separate reaction vessels can be substituted for the single reaction vessel described herein. The nucleation stage of grain preparation can be performed in an upstream reaction vessel (herein also termed a nucleation reaction vessel) and the dispersed grain nuclei can be transferred to a downstream reaction vessel in which the growth stage of grain precipitation occurs (herein also termed a growth reaction vessel). In one arrangement of this type an enclosed nucleation vessel can be employed to receive and mix reactants upstream of the growth reaction vessel, as illustrated by Posse et al U.S. Patent 3,790,386, Forster et al U.S. Patent 3,897,935, Finnicum et al U.S. Patent 4,147,551, and Verhille et al U.S. Patent 4,171,224, 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 hereinbefore in terms of utilizing iodide to produce the crystal irregularities required for tabular grain formation, alternative nucleation procedures have been devised, as demonstrated in the following Examples, that eliminate any requirement of iodide ion being present during nucleation in order to produce tabular grains. These alternative procedures are, further, compatible with the use of iodide during nucleation. Thus, these procedures can be relied upon entirely during nucleation for tabular grain formation or can be relied upon in combination with iodide ion during nucleation to produce tabular grains.

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

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

The emulsions of the invention include silver chloride emulsions, 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 novel precipitation process 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 those that contain more than 70 mole percent (optimally more than 90 mole percent) chloride.

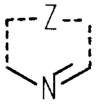
Although not essential, a further procedure that can be employed to maximize the population of tabular grains having {100} major faces is to incorporate an agent capable of restraining the emergence of non-{100} grain crystal faces in the emulsion during its preparation. The restraining agent, when employed, 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 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 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)

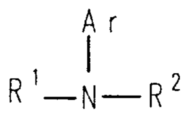


where

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)



$$R^1-\underset{}{\overset{\overset{\textstyle Ar}{|}}{N}}-R^2$$

where

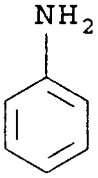
Ar is an aromatic ring structure containing from 5 to 14 carbon atoms and

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.

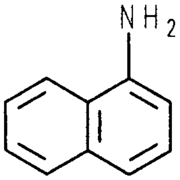
The following are representative of compounds contemplated satisfying formulae I and/or II:

RA-1



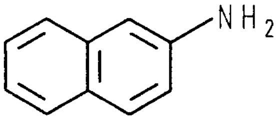
aniline

RA-2



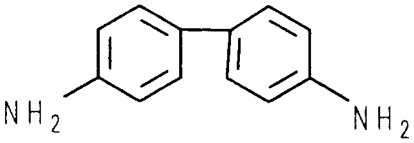
a-naphthylamine

RA-3



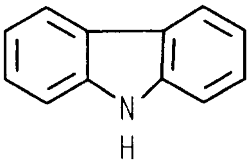
b-naphthylamine

RA-4



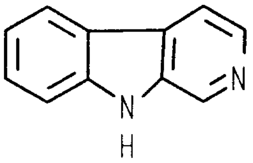
benzidine

RA-5



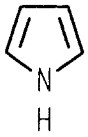
carbazole

RA-6



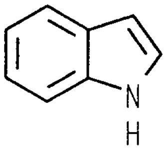
norharman

RA-7



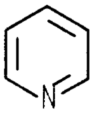
pyrrole

RA-8



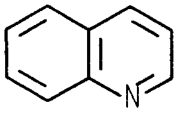
indole

RA-9



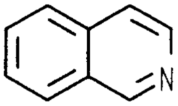
pyridine

RA-10



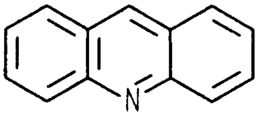
quinoline

RA-11



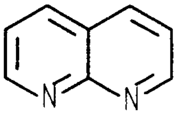
isoquinoline

RA-12



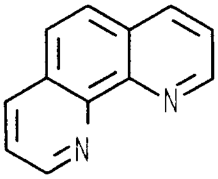
acridine

RA-13



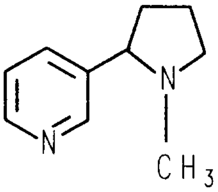
1,8-naphthyridine

RA-14



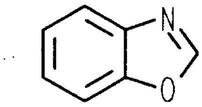
1,10-phenanthroline

RA-15



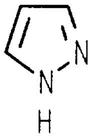
nicotine

RA-16



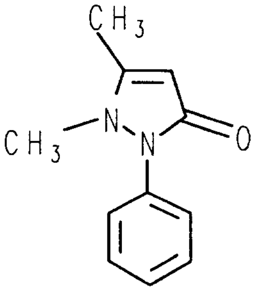
benzoxazole

RA-17



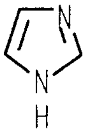
pyrazole

RA-18



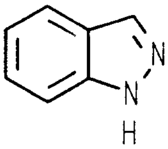
antipyrine

RA-19



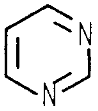
imidazole

RA-20



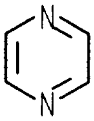
indazole

RA-21



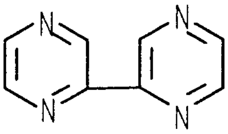
pyrimidine

RA-22



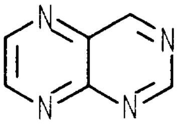
pyrazine

RA-23



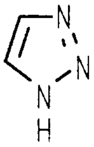
2,2'-bipyrazine

RA-24



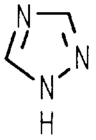
pteridine

RA-25



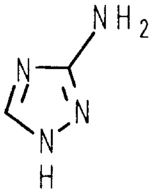
1,2,3-triazole

RA-26



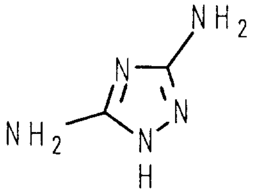
1,2,4-triazole

RA-27



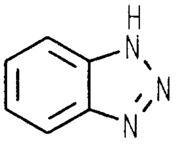
3-amino-1,2,4-triazole

RA-28



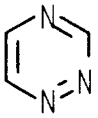
3,5-diamino-1,2,4-triazole

RA-29



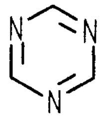
benzotriazole

RA-30



1,2,4-triazine

RA-31



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 here incorporated by reference.

The emulsions of this invention can be chemically sensitized with active gelatin as illustrated by T. H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, pp. 67-76, or with sulfur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, rhenium or phosphorus sensitizers or combinations of these sensitizers, (particularly combinations of sulfur with gold or selenium), such as at pAg levels of from 5 to l0, pH levels of from 5 to 8 and temperatures of from 30 to 80 °C, as illustrated by *Research Disclosure*, Vol. l20, April, 1974, Item l2008, *Research Disclosure*, Vol. l34, June, 1975, Item l3452, Sheppard et al U.S. Patent l,623,499, Matthies et al U.S. Patent l,673,522, Waller et al U.S. Patent 2,399,083, Damschroder et al U.S. Patent 2,642,36l, McVeigh U.S. Patent 3,297,447, Dunn U.S. Patent 3,297,446, McBride U.K. Patent 1,315,755, Berry et al U.S. Patent 3,772,03l, Gilman et al U.S. Patent 3,76l,267, Ohi et al U.S. Patent 3,857,711, Klinger et al U.S. Patent 3,565,633, Oftedahl U.S. Patents 3,901,714 and 3,904,4l5 and Simons U.K. Patent l,396,696; chemical sensitization being optionally conducted in the presence of thiocyanate derivatives as described in Damschroder U.S.Patent 2,642,36l; thioether compounds as disclosed in Lowe et al U.S. Patent 2,52l,926, Williams et al U.S. Patent 3,02l,2l5 and Bigelow U.S. Patent 4,054,457; and azaindenes, azapyridazines and azapyrimidines as described in Dostes U.S. Patent 3,411,914, Kuwabara et al U.S. Patent 3,554,757, Oguchi et al U.S. Patent 3,565,63l and Oftedahl U.S. Patent 3,901,714; elemental sulfur as described by Miyoshi et al European Patent Application EP 294,149 and Tanaka et al European Patent Application EP 297,804; and thiosulfonates as described by Nishikawa et al European Patent Application EP 293,917. Additionally or alternatively, the emulsions can be reduction-sensitized--e.g., with hydrogen, as illustrated by Janusonis U.S. Patent 3,89l,446 and Babcock et al U.S. Patent 3,984,249, by low pAg (e.g., less than 5), high pH (e.g., greater than 8) treatment, or through the use of reducing agents such as stannous chloride, thiourea dioxide, polyamines and amineboranes as illustrated by Allen et al U.S. Patent 2,983,609, Oftedahl et al *Research Disclosure*, Vol. l36, August, 1975, Item l3654, Lowe et al U.S. Patents 2,5l8,698 and 2,739,060, Roberts et al U.S. Patents 2,743,l82 and 'l83, Chambers et al U.S. Patent 3,026,203 and Bigelow et al U.S. Patent 3,36l,564.

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

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

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

The merocyanine spectral sensitizing dyes include, joined by a methine linkage, a basic heterocyclic nucleus of the cyanine-dye type and an acidic nucleus such as can be derived from barbituric acid, 2-thiobarbituric acid, rhodanine, hydantoin, 2-thiohydantoin, 4-thiohydantoin, 2-pyrazolin-5-one, 2-isoxazolin-5-one, indan-1,3-dione, cyclohexan-1,3-dione, 1,3-dioxane-4,6-dione, pyrazolin-3,5-dione, pentan-2,4-dione, alkylsulfonyl acetonitrile, benzoylacetonitrile, malononitrile, malonamide, isoquinolin-4-one, chroman-2,4-dione, 5H-furan-2-one, 5H-3-pyrrolin-2-one, 1,1,3-tricyanopropene and telluracyclohexanedione.

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

Combinations of spectral sensitizing dyes can be used which result in supersensitization--that is, spectral sensitization greater in some spectral region than that from any concentration of one of the dyes alone or that which would result from the additive effect of the dyes. Supersensitization can be achieved with selected combinations of spectral sensitizing dyes and other addenda such as stabilizers and antifoggants, development accelerators or inhibitors, coating aids, brighteners and antistatic agents. Any one of several mechanisms, as well as compounds which can be responsible for supersensitization, are discussed by Gilman, *Photographic Science and Engineering*, Vol. l8, 1974, pp. 4l8-430.

Spectral sensitizing dyes can also affect the emulsions in other ways. For example, spectrally sensitizing dyes can increase photographic speed within the spectral region of inherent sensitivity. Spectral sensitizing dyes can also function as antifoggants or stabilizers, development accelerators or inhibitors, reducing or nucleating agents, and halogen acceptors or electron acceptors, as disclosed in Brooker et al U.S. Patent 2,131,038, Illingsworth et al U.S. Patent 3,501,310, Webster et al U.S. Patent 3,630,749, Spence et al U.S. Patent 3,7l8,470 and Shiba et al U.S. Patent 3,930,860.

Among useful spectral sensitising dyes for sensitizing the emulsions described herein are those found in U.K. Patent 742,112, Brooker U.S. Patents l,846,300, '30l, '302, '303, '304, 2,078,233 and 2,089,729, Brooker et al U.S. Patents 2,l65,338, 2,2l3,238, 2,493,747, '748, 2,526,632, 2,739,964 (Reissue 24,292), 2,778,823, 2,917,516, 3,352,857, 3,411,916 and 3,431,111, Sprague U.S. Patent 2,503,776, Nys et al U.S. Patent 3,282,933, Riester U.S. Patent 3,660,l02, Kampfer et al U.S. Patent 3,660,l03, Taber et al U.S.

Patents 3,335,0l0, 3,352,680 and 3,384,486, Lincoln et al U.S. Patent 3,397,98l, Fumia et al U.S. Patents 3,482,978 and 3,623,88l, Spence et al U.S. Patent 3,7l8,470 and Mee U.S. Patent 4,025,349, the disclosures of which are here incorporated by reference. Examples of useful supersensitizing-dye combinations, of non-light-absorbing addenda which function as supersensitizers or of useful dye combinations are found in McFall et al U.S. Patent 2,933,390, Jones et al U.S. Patent 2,937,089, Motter U.S. Patent 3,506,443 and Schwan et al U.S. Patent 3,672,898, the disclosures of which are here incorporated by reference.

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

The following illustrate specific spectral sensitizing dye selections:

SS-1
Anhydro-5'-chloro-3'-di-(3-sulfopropyl)naphtho[1,2-d]thiazolothiacyanine hydroxide, sodium salt
SS-2
Anhydro-5'-chloro-3'-di-(3-sulfopropyl)naphtho[1,2-d]oxazolothiacyanine hydroxide, sodium salt
SS-3
Anhydro-4,5-benzo-3'-methyl-4'-phenyl-1-(3-sulfopropyl)naphtho[1,2-d]thiazolothiazolocyanine hydroxide
SS-4
1,1'-Diethylnaphtho[1,2-d]thiazolo-2'-cyanine bromide
SS-5
Anhydro-1,1'-dimethyl-5,5'-di-(trifluoromethyl)-3-(4-sulfobutyl)-3'-(2,2,2-trifluoroethyl)-benzimidazolocarbocyanine hydroxide
SS-6
Anhydro-3,3'-(2-methoxyethyl)-5,5'-diphenyl-9-ethyloxacarbocyanine, sodium salt
SS-7
Anhydro-11-ethyl-1,1'-di-(3-sulfopropyl)naphtho[1,2-d]oxazolocarbocyanine hydroxide, sodium salt
SS-8
Anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)oxaselenacarbocyanine hydroxide, sodium salt
SS-9
5,6-Dichloro-3',3'-dimethyl-1,1',3-triethylbenzimidazolo-3H-indolocarbocyanine bromide
SS-10
Anhydro-5,6-dichloro-1,1-diethyl-3-(3-sulfopropylbenzimidazolooxacarbocyanine hydroxide
SS-11
Anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(2-sulfoethylcarbamoylmethyl)thiacarbocyanine hydroxide, sodium salt
SS-12
Anhydro-5',6'-dimethoxy-9-ethyl-5-phenyl-3-(3-sulfobutyl)-3'-(3-sulfopropyl)oxathiacarbocyanine hydroxide, sodium salt
SS-13
Anhydro-5,5'-dichloro-9-ethyl-3-(3-phosphonopropyl)-3'-(3-sulfopropyl)thiacarbocyanine hydroxide

SS-14

Anhydro-3,3'-di-(2-carboxyethyl)-5,5'-dichloro-9-ethylthiacarbocyanine bromide

SS-15

Anhydro-5,5'-dichloro-3-(2-carboxyethy])-3'-(3-sulfopropyl)thiacyanine sodium salt

SS-16

9-(5-Barbituric acid)-3,5-dimethyl-3'-ethyltellurathiacarbocyanine bromide

SS-17

Anhydro-5,6-methylenedioxy-9-ethyl-3-methyl-3'-(3-sulfopropyl)tellurathiacarbocyanine hydroxide

SS-18

3-Ethyl-6,6'-dimethyl-3'-pentyl-9.11-neopentylenethiadicarbocyanine bromide

SS-19

Anhydro-3-ethyl-9,11-neopentylene-3'-(3-sulfopropyl)thiadicarbocyanine hydroxide

SS-20

Anhydro-3-ethyl-11,13-neopentylene-3'-(3-sulfopropyl)oxathiatricarbocyanine hydroxide, sodium salt

SS-21

Anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt

SS-22

Anhydro-5,5'-diphenyl-3,3'-di-(3-sulfobutyl)-9-ethyloxacarbocyanine hydroxide, sodium salt

SS-23

Anhydro-5,5'-dichloro-3,3'-di-(3-sulfopropyl)-9-ethylthiacarbocyaninehydroxide, triethylammonium salt

SS-24

Anhydro-5,5'-dimethyl-3,3'-di-(3-sulfopropyl)-9-ethylthiacarbocyaninehydroxide, sodium salt

SS-25

Anhydro-5,6-dichloro-1-ethyl-3-(3-sulfobutyl)-1'-(3-sulfopropyl)benzimidazolonaphtho[1,2-d]-thiazolocarbocyanine hydroxide, triethylammonium salt

SS-26

Anhydro-11-ethyl-1,1'-di-(3-sulfopropyl)naphth[1,2-d]oxazolocarbocyanine hydroxide, sodium salt

SS-27

Anhydro-3,9-diethyl-3'-methylsulfonylcarbamoylmethyl-5-phenyloxathiacarbocyanine *p*-toluenesulfonate

SS-28

Anhydro-6,6'-dichloro-1,1'-diethyl-3,3'-di-(3-sulfopropyl)-5,5'-bis(trifluoromethyl)-benzimidazolocarbocyanine hydroxide, sodium salt

SS-29

Anhydro-5'-chloro-5-phenyl-3,3'-di-(3-sulfopropyl)oxathiacyanine hydroxide, sodium salt

SS-30

Anhydro-5,5'-dichloro-3,3'-di-(3-sulfopropyl)thiacyanine hydroxide, sodium salt

SS-31

3-Ethyl-5-[1,4-dihydro-1-(4-sulfobutyl)pyridin-4-yl-idene]rhodanine, triethylammonium salt

SS-32

1-Carboxyethyl-5-[2-(3-ethylbenzoxazolin-2-ylidene)ethylidene]-3-phenylthiohydantoin

SS-33

4-[2-((1,4-Dihydro-1-dodecylpyridin-ylidene)ethyl-idene]-3-phenyl-2-isoxasolin-5-one

SS-34

5-(3-Ethylbenzoxazolin-2-ylidene)-3-phenylrhodanine

SS-35

1,3-Diethyl-5-{[1-ethyl-3-(3-sulfopropyl)benzimidazolin-2-yliderie]ethylidene}-2-thiobarbituric acid

SS-36

5-[2-(3-Ethylbenzoxazolin-2-ylidene)ethylidene]-1-methyl-2-dimethylamino-4-oxo-3-phenylimidazolinium *p*-toluenesulforate

SS-37

5-[2-(5-Carboxy-3-methylbenzoxazolin-2-ylidene)ethylidene]-3-cyano-4-phenyl-1-(4-methylsulfonamido-3-pyrrolin-5-one

SS-38

2-[4-(Hexylsulfonamido)benzoylcyanomethine]-2-{2-{3-(2-methoxyethyl)-5-[(2-methoxyethyl)sulfonamido]-benzoxazolin-2-ylidene}ethylidene}acetonitrile

SS-39

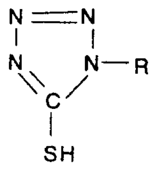
3-Methyl-4-[2-(3-ethyl-5,6-dimethylbenzotellurazolin-2-yl-idene)ethylidene]-1-phenyl-2-pyrazolin-5-one

SS-40
3-Heptyl-1-phenyl-5-{4-[3-(3-sulfobutyl)-naphtho[1,2-d]thiazolin]-2-butenylidene}-2-thiohydantoin
SS-41
1,4-Phenylene-bis(2-aminovinyl-3-methyl-2-thiazolinium] dichloride
SS-42
Anhydro-4-{2-[3-(3-sulfopropyl)thiazolin-2-ylidene]ethylidene}-2-{3-[3-(3-sulfopropyl)thiazolin-2-ylidene]-propenyl-5-oxazolium, hydroxide, sodium salt
SS-43
3-Carboxymethyl-5-{3-carboxymethyl-4-oxo-5-methyl1,3,4-thiadiazolin-2-ylidene)ethylidene]thiazolin-2-ylidene}rhodanine, dipotassium salt
SS-44
1,3-Diethyl-5-[1-methyl-2-(3,5-dimethylbenzotellurazolin-2-ylidene)ethylidene]-2-thiobarbituric acid
SS-45
3-Methyl-4-[2-(3-ethyl-5,6-dimethylbenzotellurazolin-2-ylidene)-1-methylethylidene]-1-phenyl-2-pyrazolin-5-one
SS-46
1,3-Diethyl-5-[1-ethyl-2-(3-ethyl-5,6-dimethoxybenzotellurazolin-2-ylidene)ethylidene]-2-thiobarbituric acid
SS-47
3-Ethyl-5-{[(ethylbenzothiazolin-2-ylidene)-methyl][(1,5-dimethylnaphtho[1,2-d]selenazolin-2-ylidene)-methyl]methylene}rhodanine
SS-48
5-{Bis[(3-ethyl-5,6-dimethylbenzothiazolin-2-ylidene)methyl]methylene}-1,3-diethyl-barbituric acid
SS-49
3-Ethyl-5-{[(3-ethyl-5-methylbenzotellurazolin-2-ylidene)methyl][1-ethylnaphtho[1,2-d]-tellurazolin-2-ylidene)methyl]methylene)rhodanine
SS-50
Anhydro-5,5'-diphenyl-3,3'-di-(3-sulfopropyl)thia-cyanine hydroxide, triethylammonium salt
SS-51
Anhydro-5-chloro-5'-phenyl-3,3'-di-(3-sulfopropyl)thiacyanine hydroxide, triethylammonium salt

The Group A photographic stabilizers employed in the practice of this invention are mercapto heterocyclic nitrogen compounds containing a mercapto group bonded to a carbon atom which is linked to an adjacent nitrogen atom in a heterocyclic ring system. Typical Group A stabilizers are heterocyclic mercaptans such as mercaptotetrazoles, for example a 5-mercaptotetrazole, and more particularly, an aryl 5-mercaptotetrazole such as a phenyl 5-mercaptotetrazole. Suitable Group A stabilizers that can be employed are described in the following documents, the disclosures of the U.S. patents which are hereby incorporated herein by reference: mercaptotetrazoles, -triazoles and -diazoles as illustrated by Kendall, U.S. Patent No. 2,403,927, Kennard et al. U.S. Patent No. 3,266,897, *Research Disclosure*, Vol. 116, December 1973, Item 11684, Luckey et al. U.S. Patent No. 3,397,987, Salesin U.S. Patent No. 3,708,303 and purines as illustrated by Sheppard et al., U.S Patent No. 2,319,090.

The heterocyclic ring system of the Group A stabilizers can contain one or more heterocyclic rings wherein the heterocyclic atoms (i.e., atoms other than carbon, including nitrogen, oxygen, sulfur, selenium and tellurium) are members of at least one heterocyclic ring. A heterocyclic ring in a ring system can be fused or condensed to one or more rings that do not contain heterocyclic atoms. Suitable heterocyclic ring systems include the monoazoles (e.g., oxazoles, benzoxazoles, selenazoles, benzothiazoles), diazoles (e.g., imidazoles, benzimidazoles, oxadiazoles and thiadiazoles), triazoles (e.g., 1,2,4-triazoles, especially those containing an amino substituent in addition to the mercapto group), pyrimidines, 1,2,4-triazines, s-triazines, and azaindenes (e.g., tetraazaindenes). It is understood that the term mercapto includes the undissociated thioenol or tautomeric thiocarbonyl forms, as well as the ionized, or salt forms. When the mercapto group is in a salt form, it is associated with a cation of an alkali metal such as sodium or potassium, or ammonium, or a cationic derivative of such amines as triethylamine, triethanolamine, or morpholine.

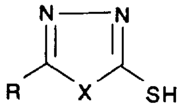
Any of the mercapto heterocyclic nitrogen compounds, as described herein, will act as stabilizers in the practice of this invention. However, particularly good results are obtained with the mercapto azoles, especially the 5-mercapto tetrazoles. 5-Mercapto tetrazoles which can be employed include those having the structure:



(A-I)

where R is an aliphatic or aromatic radical containing up to 20 carbon atoms. The alkyl or aryl radicals comprising R may be unsubstituted or substituted. Suitable substituents include, for example, alkoxy, phenoxy, halogen, cyano, nitro, amino, substituted amino, sulfo, sulfamyl, substituted sulfamyl, sulfonylphenyl, sulfonylalkyl, fluosulfonyl, sulfonamidophenyl, sulfonamidoalkyl, carboxy, carboxylate, ureido carbamyl, carbamylphenyl, carbamylalkyl, carbonylalkyl, and carbonylphenyl.

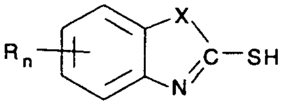
Some thiadiazole or oxadiazole Group A stabilizers that can be employed in the practice of this invention can be represented by the following structure:



(A-II)

where X is S or O, and R is as defined in Formula (A-I) hereinbefore.

Some benzoxazole Group A stabilizers that can be employed in the practice of this invention can be represented by the following structure:



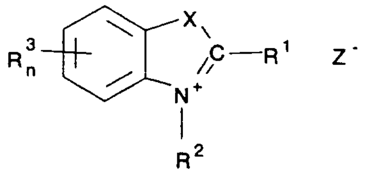
(A-III)

where X is O, S or Se, R is alkyl containing up to four carbon atoms, such as methyl, ethyl, propyl, butyl; alkoxy containing up to four carbon atoms, such as methoxy, ethoxy, butoxy; halogen, such as chloride or bromide, cyano, amido, sulfamido or carboxy, and n is 0 to 4.

Examples of Group A photographic stabilizers useful in the practice of this invention are 1-(3-acetamidophenyl)-5-mercaptotetrazole, 1-phenyl-5-mercaptotetrazole, 1-(3-methoxyphenyl)-5-mercaptotetrazole, 1-(3-ureidophenyl)-5-mercaptotetrazole, 1-(3-N-carboxymethyl)ureidophenyl)-5-mercaptotetrazole, 1-(3-N-ethyl oxalamido)phenyl)-5-mercaptotetrazole, 1-(4-ureidophenyl)-5-mercaptotetrazole, 1-(4-acetamidophenyl)-5-mercaptotetrazole, 1-(4-methoxyphenyl)-5-mercaptotetrazole, 1-(4-carboxyphenyl)-5-mercaptotetrazole, 1-(4-chlorophenyl)-5-mercaptotetrazole, 2-mercapto-5-phenyl-1,3,4-oxadiazole, 2-mercapto-5-(4-acetamidophenyl)-1,3,4-oxadiazole, 2-mercapto-5-phenyl-1,3,4-thiadiazole, 2-mercapto-5-(4-ureidophenyl)-1,3,4-thiadiazole, 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 2-mercaptobenzoselenazole, 2-mercapto-5-methylbenzoxazole, 2-mercapto-5-methoxybenzoxazole, 2-mercapto-6-chlorobenzothiazole and 2-mercapt-6-methylbenzothiazole.

The Group B photographic stabilizers are quaternary aromatic chalcogenazolium salts wherein the chalcogen is sulfur, selenium or tellurium. Typical Group B stabilizers are azolium salts such as benzothiazolium salts, benzoselenazolium salts and benzotellurazolium salts. Charge balancing counter ions for such salts include a wide variety of negatively charged ions, as well known in the photographic art, and exemplified by chloride, bromide, iodide, perchlorate, benzenesulfonate, propylsulfonate, toluenesulfonate, tetrafluoroborate, hexafluorophosphate and methyl sulfate. Suitable Group B stabilizers that can be employed are described in the following U.S. patents, the disclosures of which are hereby incorporated herein by reference: quaternary ammonium salts of the type illustrated by Allen et al. U.S. Patent No. 2,694,716, Brooker et al. U.S. Patent No. 2,131,038, Graham U.S. Patent No. 3,342,596, Arai et al. U.S. Patent No. 3,954,478 and Przyklek-Elling U.S. Patent No. 4,661,438.

Some Group B stabilizers that may be employed in the practice of this invention can be represented by the following structure:



(B)

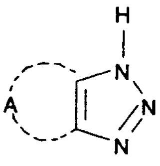
where X is S, Se or Te, R^1 is hydrogen where X is S, and is methyl where X is Se or Te, R^2 is alkyl or alkenyl containing up to four carbon atoms, such as methyl, ethyl, propyl, propenyl; substituted alkyl containing up to four carbon atoms, such as sulfopropyl or sulfamylmethyl, R^3 is alkyl containing up to four carbon atoms, such as methyl, propyl, butyl; alkoxy containing up to four carbon atoms such as ethoxy or propoxy; halogen, cyano, amido, sulfamido or carboxy; n is 0-2, and Z is a counter ion, such as halogen, benzenesulfonate or tetrafluoroborate.

Examples of useful Group B photographic stabilizers include 2-methyl-3-ethylbenzoselenazolium p-toluenesulfonate, 3-[2-(N-methylsulfonyl)carbamoylethyl]-benzothiazolium tetrafluoroborate, 3,3'-decamethylene-bis-(benzothiazolium) bromide, 3-methylbenzothiazolium hydrogen sulfate, 3-allylbenzothiazolium tetrafluoroborate, 5,6-dimethoxy-3-sulfopropylbenzothiazolium salt, 5-chloro-3-methylbenzothiazolium tetrafluoroborate, 5,6-dichloro-3-ethylbenzothiazolium tetrafluoroborate, 5-methyl-3-allylbenzothiazolium tetrafluoroborate, 2-methyl-3-ethylbenzotellurazolium tetrafluoroborate, 2-methyl-3-allylbenzotellurazolium tetrafluoroborate, 2-methyl-3-allyl-5-chlorobenzoselenazolium tetrafluoroborate, 2-methyl-3-allyl-5-chlorobenzoselenazolium tetrafluoroborate and 2-methyl-3-allyl-5,6-dimethoxybenzoselenazolium p-toluenesulfonate.

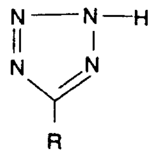
The Group C photographic stabilisers are triazoles or tetrazoles which contain an ionizable (or dissociable) hydrogen bonded to a nitrogen atom in a heterocyclic ring system. Such a hydrogen atom is ioniizable under normal conditions of preparation, storing or processing of the high chloride {100} tabular grain emulsions of this invention. The triazole or tetrazole ring can be fused to one or more aromatic, including heteroaromatic, rings containing 5 to 7 ring atoms to provide a heterocyclic ring system. Such heterocyclic ring systems include, for example, benzotriazoles, naphthotriazoles, tetraazaindenes and triazolotetrazoles. The triazole or tetrazole rings can contain substituents including lower alkyl such as methyl, ethyl, propyl, aryl containing up to 10 carbon atoms, for example, phenyl or naphthyl. Suitable additional substituents in the heterocyclic ring system include hydroxy, halogen such as chlorine, bromine, iodine; cyano, alkyl such as methyl, ethyl, propyl, trifluoromethyl; aryl such as phenyl, cyanophenyl, naphthyl, pyridyl; aralkyl such as benzyl, phenethyl; alkoxy such as methoxy, ethoxy; aryloxy such as phenoxy; alkylthio such as methylthio, carboxymethylthio; acyl such as formyl, formamidino, acetyl, benzoyl, benzenesulfonyl; carboalkoxy such as carboethoxy, carbomethoxy or carboxy.

Typical Group C stabilizers are tetrazoles, benzotriazoles and tetraazaindenes. Suitable Group C stabilizers that can be employed are described in the following documents, the disclosures of the U.S. patents which are hereby incorporated herein by reference: tetrazoles, as illustrated by P. Glafkides "Photographic Chemistry", Vol. 1, pages 375-376, Fountain Press, London, published 1958, azaindenes, particularly tetraazaindenes, as illustrated by Heimbach et al. U.S. Patent No. 2,444,605, Knott U.S. Patent No. 2,933,388, Williams et al. U.S. Patent No. 3,202,512, ***Research Disclosure***, Vol. 134, June 1975, Item 13452 and Vol. 148, August 1976, Item 14851, Nepker et al. U.K. Patent No. 1,338,567, Birr et al. U.S. Patent No. 2,152,460 and Dostes et al. French Patent No. 2,296,204.

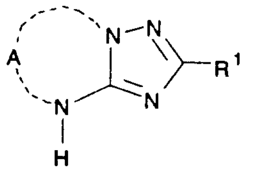
Some useful Group C stabilizers that can be employed in the practice of this invention can be represented by the following structures:



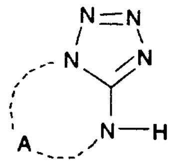
(C-I)



(C-II)



(C-III)



(C-IV)

where R is lower alkyl such as methyl, ethyl, propyl, butyl; or aryl containing up to 10 carbon atoms such as cyanophenyl or naphthyl; R^{1}' in addition to being the same as R, can also be hydrogen; alkoxy containing up to 8 carbon atoms, such as methoxy, ethoxy, butoxy, octyloxy; alkylthio containing up to 8 carbon atoms, such as methylthio, propylthio, pentylthio, octylthio; or aryloxy or arylthio containing up to 10 carbon atoms; and A represents the non-metallic atoms necessary to complete a 5- to 7- membered aromatic ring which can be substituted with, for example, hydroxy, halogen such as chlorine, bromine, iodine; cyano, alkyl such as methyl, ethyl, propyl, trifluoromethyl; aryl such as phenyl, cyanophenyl, naphthyl, pyridyl; aralkyl such as benzyl, phenethyl; alkoxy such as methoxy, ethoxy; aryloxy such as phenoxy; alkylthio such as methylthio, carboxymethylthio; acyl such as formyl, acetyl, benzoyl; alkylsulfonyl or arylsulfonyl, such as methanesulfonyl or benzenesulfonyl; carboalkoxy such as carboethoxy, carbomethoxy; or carboxy.

Typical useful Group C photographic stabilizers include 5-chlorobenzotriazole, 5,6-dichlorobenzotriazole, 5-cyanobenzotriazole, 5-trifluoromethylbenzotriazole, 5,6-diacetylbenzotriazole, 5-(p-cyanophenyl)tetrazole, 5-(p-trifluoromethylphenyl)tetrazole, 5-(1-naphthyl)tetrazole, 5-(2-pyridyl)tetrazole, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene sodium salt, 5-bromo-4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene sodium salt, 4-hydroxy-6-methyl-2-methylthio-1,3,3a,7-tetraazaindene sodium salt, 5-bromo-4-hydroxy-6-methyl-2-octylthio-1,3,3a,7-tetraazaindene sodium salt.

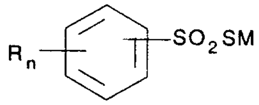
The Group D photographic stabilizers are dichalcogenide compounds comprising an -X-X- linkage between carbon atoms wherein each X is divalent sulfur, selenium or tellurium. Typical Group D stabilizers are organic disulfides, diselenides and ditellurides where the chalcogen joins aliphatic or aromatic groups or are part of a ring system. Suitable Group D stabilizers that can be employed are described in the following documents, the disclosures of the U.S. patents which are hereby incorporated herein by reference: diselenides as illustrated by Brown et al. U.K. Patent No. 1,336,570, Pollet et al. U.K. Patent No. 1,282,303, aromatic tellurochalcogenides, as illustrated by Gunther et al. U.S. Patent No. 4,607,000 and Lok et al. U.S. Patent No. 4,607,001, cyclic oxaspiro ditellurides, as illustrated by Lok et al. U.S. Patent No. 4,861,703, 5-thiooctic acid, as illustrated by U.S. Patent No. 2,948,614, and acylamidophenyl disulfides, as illustrated by U.S. Patent No. 3,397,986. Some useful Group D photographic stabilizers that can be employed in the practice of this invention can be represented by the following structure:

$$R{-}X{-}X{-}R^{1} \qquad (D)$$

where X is divalent S, Se or Te, R and R^{1} can be the same or different alkyl, typically containing one to four carbon atoms such as methyl, ethyl, propyl, butyl; aryl typically containing up to ten carbon atoms such as phenyl or naphthyl, and R and R^{1} together can form a 5 to 7-membered ring containing only carbon atoms in combination with the S, Se or Te atoms. Such ring can be further substituted with halogen such a chlorine, acetamido, carboxyalkyl such as carboxybutyl and alkoxy, typically containing one to four carbon atoms such as methoxy, propoxy and butoxy. Examples of useful Group D photographic stabilizers are bis-(4-acetamido)phenyl disulfide, bis-(4-glutaramido)phenyl disulfide, bis(4-oxalamido)phenyl disulfide, bis-(4-succinamido)phenyl disulfide, 6-thiooctic acid, 5-thiooctic acid, alpha,alpha-dithiodipropionic acid, beta, beta-dithiodipropionic acid, 2-oxa-6,7-diselenaspiro[3,4]octane, 2-oxa-6,7-ditelluraspiro[3,4]octane, bis-[2-(N-methylacetamido)-4,5-dimethylphenyl] ditelluride, bis-[2-(N-methylacetamido)-4-methoxyphenyl] ditelluride, bis-(2-acetamido-4-methoxyphenyl) diselenide, m-carboxyphenyl diselenide and p-cyanophenyl diselenide.

The Group E photographic stabilizers are organic compounds containing a thiosulfonyl group having the formula -SO_2SM where M is a proton or cation, preferably an alkali metal such as potassium. Typical Group E stabilizers are alkyl and aryl thiosulfonates. Suitable Group E stabilizers that can be employed have the general formula Z-SO_2S-M where Z represents alkyl, aryl or a heterocycle, and M represents hydrogen, a metal cation, e.g., a cation of an alkali metal such as sodium or potassium, organic cations such as ammonium ions and guanidium ions, as illustrated in Nishikawa et al. U.S. Patent No. 4,960,689, the disclosure of which is hereby incorporated herein by reference.

Some useful Group E stabilizers that can be employed in the practice of this invention can be represented by the following structure:



(E)

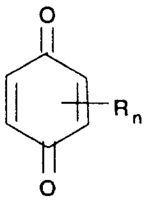
wherein R is alkyl or aryl, typically containing up to 10 carbon atoms, as exemplified by lower alkyl such as methyl, ethyl, propyl; phenyl, lower alkoxy such as ethoxy, methoxy, propoxy, pentoxy, halogen such as chlorine, nitro, amino; and carboxyl, M is a proton or a cation such as an alkali metal cation, typically sodium or potassium or an organic cation, typically ammonium or guanidinium, and n is 0 to 4.

Typical Group E photographic stabilizers include p-tolylthiosulfonate potassium salt, p-chlorophenylthiosulfonate potassium salt, 1-butylthiosulfonate potassium salt, 1,4-dithiosulfonatobutane dipotassium salt and p-methoxyphenylthiosulfonate potassium salt.

The Group F photographic stabilizers are mercuric salts. Preferred Group F stabilizers are inorganic mercury salts such as mercuric halides, as exemplified by mercuric chloride, which are readily available and conveniently employed. Examples of useful Group F stabilisers that can be employed are mercuric chloride or mercuric iodide, or mercuric salts of thiazoles, as illustrated by Allen et al. U.S. Patent No. 2,728,663 and Saleck et al. U.S. Patent No. 3,432,304, the disclosures of which are hereby incorporated herein by reference.

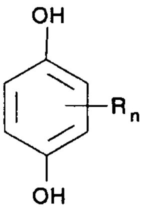
The Group G photographic stabilisers are quinone compounds. Typical examples of such oxidants are benzoquinone and napthoquinone.

Some useful Group G stabilizers that can be employed in the practice of this invention can be represented by the following structure:



where R is lower alkyl such as methyl, ethyl, butyl; aryl containing up to 10 carbon atoms, such as phenyl or naphthyl; halogen, such as chlorine, bromine, fluorine; cyano; acyl, such as acetyl or benzoyl; alkylsulfonyl or arylsulfonyl, such as methanesulfonyl or benzenesulfonyl; carboalkoxy; or carboxy; n is 0 to 4; and two R groups can combine to form an aromatic ring containing up to 10 carbon atoms, for example a benzo or naphtho ring which can contain substituents such as those just described.

The photographic stabilizers of Groups A-G can be used in combination within each group, or in combination between different groups. Enolic reducing compounds that can be used in combination with the photographic stabilizers in Group A are described in T.H. James, *The Theory of the Photographic Process*, 4th Edition, MacMillan Publishing Company, Inc., 1977, Chapter 11, Section E, developing agents of the type HO-(CH = CH)$_n$-OH, and on page 311, Section F, developing agents of the type HO-(CH = CH)$_n$-NH$_2$. Representative members of the Section E developing agents hydroquinone or catechol. Representative members of the Section F developing agents are aminophenols and the aminopyrazolones. Suitable reducing agents that can be used in combination with the photographic stabilizers in Group A are also described in European Patent Application Nos. 476 521 A2 and 482 599 A1 and East German Patent Application DD 293 207 A5. Specific examples of useful reducing compounds are piperidinohexose reductone, 4,5-dihydroxybenzene-1,3-disulfonic acid (catecholdisulfonic acid), disodium salt, 4-(hydroxymethyl)-4-methyl-1-phenyl-3-pyrazolidinone, and hydroquinone compounds. Typical hydroquinones or hydroquinone derivatives that can be used in the combination described can be represented by the following structure:



where R is the same or different and is alkyl such as methyl, ethyl, propyl, butyl, octyl; aryl such as phenyl, and contains up to 20 carbon atoms, typically 6-20 carbon atoms, or is -L-A where L is a divalent linking group such as oxygen, sulfur or amido, and A is a group which enhances adsorption onto silver halide grains such as a thionamido group, a mercapto group, a group containing a disulfide linkage or a 5- or 6-membered nitrogen-containing heterocyclic group and n is 0-2. Beneficial results can also be achieved using the photographic stabilizers of Group E in combination with salts of aryl sulfinates such as tolylsulfinate sodium salt, typically in a weight ratio in range of about 1:10 to 10:1.

The photographic stabilizers used in the practice of this invention are conveniently incorporated into the high chloride {100} tabular grain emulsions or elements comprising such emulsions just prior to coating the emulsion in the elements. However, they can be added to the emulsion at the time the emulsion is manufactured, for example, during chemical or spectral sensitization. It is generally most convenient to introduce such stabilizers after chemical ripening of the emulsion and before coating. The stabilizers can be added directly to the emulsion, or they can be added at a location within a photographic element which permits permeation to the emulsion to be protected. For example, the photographic stabilizers can be incorporated into hydrophilic colloid layers such as in an overcoat, interlayer or subbing layer just prior to coating. Any concentration of photographic stabilizer effective to protect the emulsion against changes in development fog and sensitivity can be employed. Optimum concentrations of photographic stabilizer for specific applications are usually determined empirically by varying concentrations in the manner well known to those skilled in the art. Such investigations are typically relied upon to identify effective concentrations for a specific situation. Of course, the effective concentration used will vary widely depending upon such things as the particular emulsion chosen, its intended use, storage conditions and the specific photographic stabilizer selected. Although an effective concentration for stabilizing the high chloride {100} tabular grain emulsions may vary, concentrations of at least about 0.005 millimole per silver mole in the radiation sensitive silver halide emulsion have been found to be effective in specific situations. More typically, the minimum effective amount of photographic stabilizer is at least 0.03 millimole, and frequently at least 0.3 millimole per silver mole. For many of the photographic stabilizers used in this invention, the effective concentration is in the range of about 0.06 to 0.8 and often about 0.2 to 0.5 millimole/mole silver. However, as illustrated by the following Examples, concentrations well outside of these ranges can be used.

Negative-type emulsion coatings which contain photographic stabilizers of Groups A-G can be further protected against instability by incorporation of other stabilizers, antifoggants, antikinking agents, latent-image stabilizers and similar addenda in the emulsion and contiguous layers prior to coating. Most of the antifoggants effective in the emulsions used in this manner can also be used in developers and can be classified under a few general headings, as illustrated by C.E.K. Mees, *The Theory of the Photographic Process*, 2Nd Ed., Macmillan, 1954, pp. 677-680.

To protect against such instability in the emulsion coatings, stabilizers and antifoggants that can be employed, include halide ions (e.g., bromide salts); chloropalladates and chloropalladites as illustrated by Trivelli et al U.S. Patent 2,566,263; water-soluble inorganic salts of magnesium, calcium, cadmium, cobalt, manganese and zinc as illustrated by Jones U.S. Patent 2,839,405 and Sidebotham U.S. Patent 3,488,709; azomethine desensitizing dyes as illustrated by Thiers et al U.S. Patent 3,630,744; isothiourea derivatives as illustrated by Herz et al U.S. Patent 3,220,839 and Knott et al U.S. Patent 2,5l4,650; peptide derivatives as illustrated by Maffet U.S. Patent 3,274,002; polymers of l,3-dihydroxy(and/or l,3-carbamoxy)-2-methylenepropane as illustrated by Saleck et al U.S. Patent 3,926,635. High-chloride emulsions can be stabilized by the presence, especially during chemical sensitization, of elemental sulfur as described by Miyoshi et al European published Patent Application EP 294,149 and Tanaka et al European published Patent Application EP 297,804.

Among useful stabilizers in layers containing poly(alkylene oxides) are quaternary ammonium salts of the type illustrated by Piper U.S. Patent 2,886,437; water-insoluble hydroxides as illustrated by Maffet U.S. Patent 2,953,455; phenols as illustrated by Smith U.S. Patents 2,955,037 and '038; ethylene diurea as illustrated by Dersch U.S. Patent 3,582,346; barbituric acid derivatives as illustrated by Wood U.S. Patent

3,6l7,290; boranes as illustrated by Bigelow U.S. Patent 3,725,078 and aldoximines, amides, anilides and esters as illustrated by Butler et al U.K. Patent 988,052.

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

Among stabilizers useful in layers containing synthetic polymers of the type employed as vehicles and to improve covering power are monohydric and polyhydric phenols as illustrated by Forsgard U.S. Patent 3,043,697; saccharides as illustrated by U.K. Patent 897,497 and Stevens et al U.K. Patent 1,039,471, and quinoline derivatives as illustrated by Dersch et al U.S. Patent 3,446,6l8.

Where hardeners of the aldehyde type are employed, the emulsion layers can be protected with antifoggants such as monohydric and polyhydric phenols of the type illustrated by Sheppard et al U.S. Patent 2,165,421; nitro-substituted compounds of the type disclosed by Rees et al U.K. Patent l,269,268; poly(alkylene oxides) as illustrated by Valbusa U.K. Patent 1,151,914.

Kink desensitization of the emulsions can be reduced by the incorporation of thallous nitrate as illustrated by Overman U.S. Patent 2,628,l67; compounds, polymeric lattices and dispersions of the type disclosed by Jones et al U.S. Patents 2,759,82l and '822; plasticized gelatin compositions of the type disclosed by Milton et al U.S. Patent 3,033,680; water-soluble interpolymers of the type disclosed by Rees et al U.S. Patent 3,536,49l; polymeric lattices prepared by emulsion polymerization in the presence of poly-(alkylene oxide) as disclosed by Pearson et al U.S. Patent 3,772,032, and gelatin graft copolymers of the type disclosed by Rakoczy U.S. Patent 3,837,86l.

Where the photographic element of this invention is to be processed at elevated bath or drying temperatures, as in rapid access processors, pressure desensitization and/or increased fog can be controlled by selected combinations of addenda, vehicles, hardeners and/or processing conditions as illustrated by Abbott et al U.S. Patent 3,295,976, Barnes et al U.S. Patent 3,545,97l, Yamamoto et al U.S. Patent 3,6l5,619, Brown et al U.S. Patent 3,623,873, Taber U.S. Patent 3,67l,258, Abele U.S. Patent 3,79l,830, *Research Disclosure*, Vol. 99, July, 1972, Item 9930, Florens et al U.S. Patent 3,843,364, Priem et al U.S. Patent 3,867,l52, Adachi et al U.S. Patent 3,967,965 and Mikawa et al U.S. Patents 3,947,274 and 3,954,474.

In addition to increasing the pH or decreasing the pAg of an emulsion and adding gelatin, which are known to retard latent-image fading, latent-image stabilizers can be incorporated, such as amino acids, as illustrated by Ezekiel U.K. Patents l,335,923, l,378,354, l,387,654 and 1,391,672, Ezekiel et al U.K. Patent 1,394,371, Jefferson U.S. Patent 3,843,372, Jefferson et al U.K. Patent 1,412,294 and Thurston U.K. Patent l,343,904; carbonyl-bisulfite addition products in combination with hydroxybenzene or aromatic amine developing agents as illustrated by Seiter et al U.S. Patent 3,424,583; cycloalkyl-1,3-diones as illustrated by Beckett et al U.S. Patent 3,447,926; enzymes of the catalase type as illustrated by Matejec et al U.S. Patent 3,600,l82; halogen-substituted hardeners in combination with certain cyanine dyes as illustrated by Kumai et al U.S. Patent 3,88l,933; hydrazides as illustrated by Honig et al U.S. Patent 3,386,831; hydroxy-substituted benzylidene derivatives as illustrated by Thurston U.K. Patent l,308,777 and Ezekiel et al U.K. Patents l,347,544 and l,353,527; metal-organic complexes of the type disclosed by Matejec et al U.S. Patent 3,639,l28; penicillin derivatives as illustrated by Ezekiel U.K. Patent l,389,089; combinations of iridium and rhodium compounds as disclosed by Yamasue et al U.S. Patent 3,901,713 and sydnones or sydnone imines as illustrated by Noda et al U.S. Patent 3,88l,939.

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 emulsions and photographic elements intended for color photography according to 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.

In their simplest form photographic elements of the invention employ a single silver halide emulsion layer containing high chloride {100} tabular grain emulsions and a support. It is, of course, recognized that more than one such silver halide emulsion layer can be usefully included. Where more than one emulsion layer is used, e.g., two emulsion layers, all such layers can be high chloride {100} tabular grain emulsion layers. However, the use of one or more conventional silver halide emulsion layers, including other tabular grain emulsion layers, in combination with one or more high chloride {100} tabular grain emulsion layers is specifically contemplated. It is also specifically contemplated to blend the high chloride {100} tabular grain emulsions of the present invention with each other or with conventional emulsions to satisfy specific emulsion layer requirements. Instead of blending emulsions, the same effect can usually be achieved by coating the emulsions to be blended as separate layers in an emulsion unit. For example, coating of separate emulsion layers to achieve exposure latitude is well known in the art. It is further well known in the art that increased photographic speed can be realized when faster and slower silver halide emulsions are coated in separate layers. Typically the faster emulsion layer in an emulsion unit is coated to lie nearer the exposing radiation source than the slower emulsion layer. Coating the faster and slower emulsions in the reverse layer order can change the contrast obtained. This approach can be extended to three or more superimposed emulsion layers in an emulsion unit. Such layer arrangements are specifically contemplated in the practice of this invention.

The high chloride {100} tabular grain emulsions and photographic elements of this invention can contain dye image-forming compounds and photographically useful group-releasing compounds, sometimes referred to herein simply as a "PUG-releasing compound". A dye image-forming compound is typically a coupler compound, a dye redox releaser compound, a dye developer compound, an oxichromic developer compound, or a bleachable dye or dye precursor compound. Dye redox releaser, dye developer, and oxichromic developer compounds useful in color photographic elements that can be employed in image transfer processes are described in *The Theory of the Photographic Process*, 4th edition, T.H. James, editor, Macmillan, New York, 1977, Chapter 12, Section V, and in Section XXIII of *Research Disclosure*, December 1989, Item 308119, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire, PO1O 7DQ, United Kingdom. Dye compounds useful in color photographic elements employed in dye bleach processes are described in Chapter 12, Section IV, of *The Theory of the Photographic Process*, 4th edition.

Preferred dye image-forming compounds are coupler compounds, which react with oxidized color developing agents to form colored products, or dyes. A coupler compound contains a coupler moiety COUP, which is combined with the oxidized developer species in the coupling reaction to form the dye structure. A coupler compound can additionally contain a group, called a coupling-off group, that is attached to the coupler moiety by a bond that is cleaved upon reaction of the coupler compound with oxidized color developing agent. Coupling-off groups can be halogen, such as chloro, bromo, fluoro, and iodo, or organic radicals that are attached to the coupler moieties by atoms such as oxygen, sulfur, nitrogen, phosphorus, and the like.

A PUG-releasing compound is a compound that contains a photographically useful group and is capable of reacting with an oxidized developing agent to release said group. Such a PUG-releasing compound comprises a carrier moiety and a leaving group, which are linked by a bond that is cleaved upon reaction with oxidized developing agent. The leaving group contains the PUG, which can be present either as a preformed species, or as a blocked or precursor species that undergoes further reaction after cleavage of the leaving group from the carrier to produce the PUG. The reaction of an oxidized developing agent with a PUG-releasing compound can produce either colored or colorless products.

Carrier moieties (CAR) include hydroquinones, catechols, aminophenols, sulfonamidophenols, sulfonamidonaphthols, hydrazides, and the like that undergo cross-oxidation by oxidized developing agents. A preferred carrier moiety in a PUG-releasing compound is a coupler moiety COUP, which can combine with an oxidized color developer in the cleavage reaction to form a colored species, or dye. When the carrier moiety is a COUP, the leaving group is referred to as a coupling-off group. As described previously for leaving groups in general, the coupling-off group contains the PUG, either as a preformed species or as a blocked or precursor species. The coupler moiety can be ballasted or unballasted. It can be monomeric, or it can be part of a dimeric, oligomeric or polymeric coupler, in which case more than one group containing PUG can be contained in the coupler, or it can form part of a bis compound in which the PUG forms part of a link between two coupler moieties.

The PUG can be any group that is typically made available in a photographic element in an imagewise fashion. The PUG can be a photographic reagent or a photographic dye. A photographic reagent, which upon release further reacts with components in the photographic element as described herein, is a moiety such as a development inhibitor, a development accelerator, a bleach inhibitor, a bleach accelerator, an electron transfer agent, a coupler (for example, a competing coupler, a dye-forming coupler, or a development inhibitor releasing coupler, a dye precursor, a dye, a developing agent (for example, a competing developing agent, a dye-forming developing agent, or a silver halide developing agent), a silver complexing agent, a fixing agent, an image toner, a stabilizer, a hardener, a tanning agent, a fogging agent, an ultraviolet radiation absorber, an antifoggant, a nucleator, a chemical or spectral sensitizer, or a desensitizer.

The PUG can be present in the coupling-off group as a preformed species or it can be present in a blocked form or as a precursor. The PUG can be, for example, a preformed development inhibitor, or the development inhibiting function can be blocked by being the point of attachment to the carbonyl group bonded to PUG in the coupling-off group. Other examples are a preformed dye, a dye that is blocked to shift its absorption, and a leuco dye.

A PUG-releasing compound can be described by the formula CAR-$(\mathrm{TIME})_n$-PUG, wherein (TIME) is a linking or timing group, n is 0, 1, or 2, and CAR is a carrier moiety from which is released imagewise a PUG (when n is 0) or a PUG precursor $(\mathrm{TIME})_1$-PUG or $(\mathrm{TIME})_2$-PUG (when n is 1 or 2) upon reacting with oxidized developing agent. Subsequent reaction of $(\mathrm{TIME})_1$-PUG or $(\mathrm{TIME})_2$-PUG produces PUG.

Linking groups (TIME), when present, are groups such as esters, carbamates, and the like that undergo base-catalyzed cleavage, including intramolecular nucleophilic displacement, thereby releasing PUG. Where n is 2, the (TIME) groups can be the same or different. Suitable linking groups, which are also known as timing groups, are shown in U.S. Patent Nos. 5,151,343; 5,051,345; 5,006,448; 4,409,323; 4,248,962; 4,847,185; 4,857,440; 4,857,447; 4,861,701; 5,021,322; 5,026,628, and 5,021,555, all incorporated herein by reference. Especially useful linking groups are p-hydroxphenylmethylene moieties, as illustrated in the previously mentioned U.S. Patent Nos. 4,409,323; 5,151,343 and 5,006,448, and o-hydroxyphenyl substituted carbamate groups, disclosed in U.S. Patent Nos. 5,151,343 and 5,021,555, which undergo intramolecular cyclization in releasing PUG.

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

Couplers which form cyan dyes upon reaction with oxidized color developing agents are described in such representative patents and publications as: U.S. Patent Nos. 2,772,162; 2,895,826; 3,002,836; 3,034,892; 2,474,293; 2,423,730; 2,367,531; 3,041,236; 4,333,999, "Farbkuppler-eine Literaturubersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961), and Section VII D of *Research Disclosure*, Item 308119, December 1989. Preferably such couplers are phenols and naphthols.

Couplers which form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,600,788; 2,369,489; 2,343,703; 2,311,082; 3,152,896; 3,519,429; 3,062,653; 2,908,573, "Farbkupplereine Literaturubersicht," published in Agfa Mitteilungen, Band III, pp. 126-156 (1961), and Section VII D of *Research Disclosure*, Item 308119, December 1989. Preferably such couplers are pyrazolones or pyrazolotriazoles.

Couplers which form yellow dyes upon reaction with oxidized and color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,875,057; 2,407,210; 3,265,506; 2,298,443; 3,048,194; 3,447,928, "Farbkuppler-eine Literaturubersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961), and Section VII D of *Research Disclosure*, Item 308119, December 1989. Preferably such couplers are acylacetamides, such as benzoylacetamides and pivaloylacetamides.

Couplers which form colorless products upon reaction with oxidized color developing agent are described in such representative patents as: U.K. Patent No. 861,138; U.S. Patent Nos. 3,632,345; 3,928,041; 3,958,993 and 3,961,959. Preferably, such couplers are cyclic carbonyl-containing compounds which react with oxidized color developing agents but do not form dyes.

PUG groups that are useful in the present invention include, for example:

1. PUG's which form development inhibitors upon release

PUG's which form development inhibitors upon release are described in such representative patents as U.S. Patent Nos. 3,227,554; 3,384,657; 3,615,506; 3,617,291; 3,733.201 and U.K. Pat. No. 1,450,479.

2. PUGs which are dyes, or form dyes upon release

Suitable dyes and dye precursors include azo, azomethine, azophenol, azonaphthol, azoaniline, azopyrazolone, indoaniline, indophenol, anthraquinone, triarylmethane, alizarin, nitro, quinoline, indigoid and phthalocyanine dyes or precursors of such dyes such as leuco dyes, tetrazolium salts or shifted dyes. These dyes can be metal complexed or metal complexable. Representative patents describing such dyes are U.S. Patent Nos. 3,880,658; 3,931,144; 3,932,380; 3,932,381; 3,942,987, and 4,840,884.

Suitable azo, azamethine and methine dyes are represented by the formulae in U.S. Patent No. 4,840884, col. 8, lines 1-70.

Dyes can be chosen from those described, for example, in J. Fabian and H. Hartmann, *Light Absorption of Organic Colorants*, published by Springer-Verlag Co., but are not limited thereto.

3. PUG's which are couplers

Couplers released can be nondiffusible color-forming couplers, non-color forming couplers or diffusible competing couplers. Representative patents and publications describing competing couplers are: "*On the Chemistry of White Couplers*," by W. Puschel, Agfa-Gevaert AG Mitteilungen and der Forschungs-Laboratorium der Agfa-Gevaert AG, Springer Verlag, 1954, pp. 352-367; U.S. Patent Nos. 2,998,314; 2,808,329; 2,689,793; 2,742,832; German Patent No. 1,168,769 and British Patent No. 907,274.

4. PUG's which form developing agents

Developing agents released can be color developing agents, black-and-white developing agents or cross-oxidizing developing agents. They include aminophenols, phenylenediamines, hydroquinones and pyrazolidones. Representative patents are: U.S. Patent Nos. 2,193,015; 2,108,243; 2,592,364; 3,656,950; 3,658,525; 2,751,297; 2,289,367; 2,772,282; 2,743,279; 2,753,256 and 2,304,953.

5. PUG's which are bleach inhibitors

Representative patents are U.S. Patent Nos. 3,705,801; 3,715,208; and German OLS No. 2,405,279.

6. PUG's which are bleach accelerators

PUGs representative of bleach accelerators, can be found in for example U.S. Patent Nos. 4,705,021; 4,912,024; 4,959,299; 4,705,021; 5,063,145, columns 21-22, lines 1-70; and EP Patent No. 0,193,389.

7. PUGs which are electron transfer agents (ETAs)

ETAs useful in the present invention are 1-aryl-3-pyrazolidinone derivatives which, once released, become active electron transfer agents capable of accelerating development under processing conditions used to obtain the desired dye image.

The electron transfer agent pyrazolidinone moieties which have been found to be useful in providing development acceleration function are derived from compounds generally of the type described in U S Patent Nos. 4,209,580;, 4,463,081; 4,471,045; and 4,481,287 and in published Japanese patent application No. 62-123,172. Such compounds comprise 3-pyrazolidinone structures having an unsubstituted or substituted aryl group in the l-position. Also useful are the combinations disclosed in U.S. Patent No. 4,859,578. Preferably these compounds have one or more alkyl groups in the 4- or 5-positions of the pyrazolidinone ring.

8. PUGs which are development inhibiting redox releasers (DIRRs)

DIRRs useful in the present invention include hydroquinone, catechol, pyrogallol, 1,4-naphthohydroquinone, 1,2-naphthoquinone, sulfonamidophenol, sulfonamidonaphthol and hydrazide derivatives which, once released, become active inhibitor redox releasing agents that are then capable of releasing a development inhibitor upon reaction with a nucleophile such as hydroxide ion under processing conditions used to obtain the desired dye image. Such redox releasers are represented by formula (II) in U.S. Patent No. 4,985,336; col. 3, lines 10 to 25 and formulas (III) and (IV) col. 14, line 54 to col. 17, line 11. Other redox releasers can be found in European Patent Application No. 0,285,176.

Other examples of development inhibiting redox releasers can be found in the couplers represented in for example European Patent Application 0,362,870; page 13, line 25 to page 29, line 20.

The dye image-forming compounds and 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 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.

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. Patent Nos. 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 μm. Thinner formulations of 5 to about 25 μm 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 *Research Disclosure*, December 1989, Item 308119, the disclosures of which are incorporated herein by reference.

Suitable dispersing media for the emulsions, 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 emulsions and photographic 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 other than or in addition to the Group A-G stabilizers described previously (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 elements and emulsions of this invention can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image and then processed to form a visible image, as described in

Sections XVIII and XIX of *Research Disclosure*, December 1989, Item 308119. Typically, processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in turn reacts with the couler to yield a dye. Preferred color developing agents are p-phenylenediamines. Especially preferred are 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N-ethyl-N--(methanesulfonamido)ethylaniline sulfate hydrate, 4-amino-3-methyl-N-ethyl-N--hydroxyethylaniline sulfate, 4-amino-3--(methanesulfonamido)ethyl-N,N-diethylaniline hydrochloride, and 4-amino-N-ethyl-N-(2-methoxyethyl)m-toluidine di-p-toluenesulfonic acid.

With negative-working silver halide, the processing step described above provides a negative image. The described elements are preferably processed in the known Kodak Flexicolor color process as described in, for example, the British Journal of Photography Annual of 1988, pages 196-198. To provide a positive (or reversal) image, the color development step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide but not form dye, and then uniform fogging of the element to render unexposed silver halide developable. The Kodak E-6 Process is a typical reversal process. Development is followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver or silver halide, washing, and drying.

Of course, the photographic elements used in the practice of this invention can contain any of the optional additional layers and components known to be useful in such elements in general, such as, for example, subbing layers, overcoat layers, surfactants and plasticizers, some of which are discussed in detail hereinbefore. They can be coated onto appropriate supports using any suitable technique, including, for example, those described in *Research Disclosure*, December 1989, Item 308117, Section XV Coating and Drying Procedures, the disclosure of which is incorporated herein by reference.

As previously indicated, a photographic element of the invention can comprise a single radiation-sensitive emulsion layer on a support. Particularly useful embodiments, however, are multilayer elements that contain a red light-sensitized, a green light-sensitized, and a blue light-sensitized unit, each unit containing at least one dye image-forming compound in reactive association with a radiation-sensitive silver halide emulsion.

If desired, the recording elements can be used in conjunction with an applied magnetic layer as described in *Research Disclosure*, November 1992, Item 34390.

The photographic elements containing radiation sensitive {100} tabular grain emulsions 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 invention can be better appreciated by reference to the following Examples. Examples 1-19 illustrate the preparation of radiation sensitive high chloride {100} tabular grain emulsions that can be used in the practice of this invention. Examples 20-24 illustrate that photographic elements containing layers of such emulsions can be effectively protected against significant changes in sensitivity and fog upon aging.

Example 1 - Effect of Iodide on Nucleation Step of Silver Chloride Grain Morphology

An ultrathin tabular grain silver iodochloride emulsion satisfying the requirements of this invention was prepared as follows:

A 2030 mL solution containing 1.75 percent 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, the temperature remaining at 40 °C. Following the hold, a 1.0 M silver nitrate solution and a 1.0 M NaCl solution were 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.

The preparation of the following control emulsion demonstrates the effect of omitting iodide in the precipitation of the initial grain population (nucleation).

The same precipitation procedure as that just described was used, except that 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 ration {100} tabular grains were present, but did not constitute a useful quantity of the grain population.

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

Example 2 - Preparation of Tabular Silver Iodochloride Emulsion T-1

A tabular silver iodochloride emulsion was precipitated as follows:

A 4500 mL solution containing 3.5 percent by weight of low methionine gelatin, 0.0056 mol/L of sodium chloride and 3.4 x 10^{-4} mol/L of potassium iodide was provided in a stirred reaction vessel. The contents of the reaction vessel were maintained at 40 ° C, and the pCl was 2.25.

While this solution was vigorously stirred, 90 ml of 2.0 M silver nitrate solution and 90 mL of a 1.99 M sodium chloride were added simultaneously at a rate of 180 mL/min each.

The mixture was then held for 3 minutes, the temperature remaining at 40 ° C. Following the hold, a 0.5 M silver nitrate solution and a 0.5 M sodium chloride solution were added simultaneously at 24 mL/min for 40 minutes, the pCl being maintained at 2.25. The 0.5 M silver nitrate solution and the 0.5 M sodium chloride solution were then added simultaneously with a ramped linearly increasing flow from 24 mL/min to 37.1 mL/min over 70 minutes, the pCl being maintained at 2.25. Finally, 0.75 M silver nitrate solution and 0.75 M sodium chloride solution were added at constant rate of 37.1 mL/min over 90 minutes, the pCl being maintained at 2.25. The emulsion was then washed using an ultrafiltration unit, and its final pH and pCl were adjusted to 5.5 and 1.8, respectively.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 0.06 mole percent iodide, based on silver. More than 50 percent of total grain projected area was provided by tabular grains having {100} major faces with an average ECD of 1.55 µm and an average thickness of 0.155 µm.

Example 3 - Preparation of Tabular Silver Iodochloride Emulsion T-2

A tabular silver iodochloride emulsion was precipitated as described in Example 2, except that 20 molar ppm of $K_4Ru(Cl)_6$ was added during the precipitation.

The resulting emulsion contained 0.06 mole percent iodide, based on silver. More than 50 percent of the total grain projected area was provided by tabular grains having {100} major faces, with an average ECD of 1.42 µm and an average thickness of 0.146 µm.

Example 4 - Preparation of Tabular Silver Iodochloride Emulsion T-3

A tabular silver iodochloride emulsion was precipitated as described in Example 2, then washed by ultrafiltration. Its final pH and pCl were adjusted to 5.6 and 1.8, respectively.

More than 50 percent of the total grain projected area of the resulting emulsion was provided by tabular grains having {100} major faces, with an average ECD of 1.38 µm and an average thickness of 0.148 µm. The emulsion contained 0.06 mole percent iodide, based on silver.

Example 5 - Preparation of Tabular Silver Iodochloride Emulsion T-4

A tabular silver iodochloride emulsion was precipitated as described in Example 2, then washed by ultrafiltration. The final pH and pCl were adjusted to 5.6 and 1.8, respectively.

The resulting emulsion contained 0.06 mole percent iodide, based on silver. More than 50 percent of the total grain projected area was provided by tabular grains having {100} major faces, with an average ECD of 1.61 µm and an average thickness of 0.15 µm.

Example 6 - Preparation of Tabular Silver Iodochloride Emulsion T-5

This example demonstrates an emulsion according to the invention in which 90 percent of the total grain projected area is comprised of tabular grains with {100} major faces and aspect ratios of greater than 7.5.

A 2030 mL solution containing 3.52 percent by weight low methionine gelatin, 0.0056 M sodium chloride and 1.48×10^{-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 2.25.

While this solution was vigorously stirred, 30 mL of 2.0 M silver nitrate solution and 30 mL of a 1.99 M sodium chloride and 0.01 M potassium iodide solution were added simultaneously at a rate of 60 mL/min each. This achieved grain nucleation to form crystals with an initial iodide concentration of 1 mole percent, based on total silver.

The mixture was then held for 10 minutes, the temperature remaining at 40 °C. Following the hold, a 0.5 M silver nitrate solution and a 0.5 M NaCl solution were added simultaneously at 8 mL/min for 40 minutes with the pCl being maintained at 2.25. The 0.5 M $AgNO_3$ solution and the 0.5 M NaCl solution were then added simultaneously with a ramped linearly increasing flow from 8 mL per minute to 16 mL per minute over 130 minutes with the pCl maintained at 2.25.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 0.06 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 1.86 µm and an average thickness of 0.082 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 24 and an average tabularity (ECD/t^2) of 314. The ratio of major face edge lengths of the selected tabular grains was 1.2. Ninety three 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 1.47 µm, a mean thickness of 0.086 µm, a mean aspect ratio of 17.5 and a mean tabularity of 222.

Example 7 - Preparation of Tabular Silver Iodochloride Emulsion T-6

This example demonstrates an emulsion prepared similarly to the emulsion of Example 6, but an initial 0.08 mole percent iodide and a final 0.04 percent iodide.

A 2030 mL solution containing 3.52 percent by weight low methionine gelatin, 0.0056 M sodium chloride and 3.00×10^{-5} 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 2.25.

While this solution was vigorously stirred, 30 mL of 5.0 M silver nitrate solution and 30 mL of a 4.998 M sodium chloride and 0.002 M potassium iodide solution were added simultaneously at a rate of 60 mL/min each. This achieved grain nucleation to form crystals with an initial iodide concentration of 0.08 mole percent, based on total silver.

The mixture was then held for 10 minutes, the temperature remaining at 40 °C. Following the hold, a 0.5 M silver nitrate solution and a 0.5 M sodium chloride solution were added simultaneously at 8 mL/min for 40 minutes with the pCl being maintained at 2.25.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 0.04 mole percent iodide, based on silver. Fifty percent of the total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.67 µm and an average thickness of 0.035 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 20 and an average tabularity (ECD/t^2) of 651. The ratio of major face edge lengths of the selected tabular grains was 1.9. Fifty 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 0.63 µm, a mean thickness of 0.036 µm, a mean aspect ratio of 18.5 and a mean tabularity of 595.

Example 8- Preparation of Tabular Silver Iodochloride Emulsion T-7

This example demonstrates an emulsion in which the initial grain population contained 6.0 mole percent iodide and the final emulsion contained 1.6 percent iodide.

A 2030 mL solution containing 3.52 percent by weight low methionine gelatin, 0.0056 M sodium chloride and 3.00 x 10^{-5} 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 2.25.

While this solution was vigorously stirred, 30 mL of 1.0 M silver nitrate solution and 30 mL of a 0.97 M sodium chloride and 0.03 M potassium iodide solution were added simultaneously at a rate of 60 mL/min each. This achieved grain nucleation to form crystals with an initial iodide concentration of 6.0 mole percent, based on total silver.

The mixture was then held for 10 minutes, the temperature remaining at 40 °C. Following the hold, a 1.00 M silver nitrate solution and a 1.00 M sodium chloride solution were added simultaneously at 2 mL/min for 40 minutes with the pCl being maintained at 2.25.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 1.6 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 0.57 μm and an average thickness of 0.036 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 16.2 and an average tabularity (ECD/t^2) of 494. The ratio of major face edge lengths of the selected tabular grains was 1.9. Sixty 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 0.55 μm, a mean thickness of 0.041 μm, a mean aspect ratio of 14.5 and a mean tabularity of 421.

Example 9 - Preparation of Tabular Silver Iodochloride Emulsion T-8

This example demonstrates an ultrathin high aspect ratio {100} tabular grain emulsion in which 2 mole percent iodide is present in the initial population and additional iodide is added during growth to make the final iodide level 5 mole percent.

A 2030 mL solution containing 1.75 percent by weight low methionine gelatin, 0.0056 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 2.3.

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 90 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 for 10 minutes, the temperature remaining at 40 °C. Following the hold, a 1.00 M silver nitrate solution and a 1.00 M sodium chloride solution were added simultaneously at 8 mL/min while a 3.75 X 10^{-3} M potassium iodide was simultaneously added at 14.6 mL/min for 10 minutes with the pCl being maintained at 1.95.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 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 0.58 μm and an average thickness of 0.030 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 less than 10. The selected tabular grain population had an average aspect ratio (ECD/t) of 20.6 and an average tabularity (ECD/t^2) of 803. The ratio of major face edge lengths of the selected tabular grains was 2. Eighty seven 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 0.54 μm, a mean thickness of 0.033 μm, a mean aspect ratio of 17.9 and a mean tabularity of 803.

Example 10 - Preparation of Tabular Silver Iodobromochloride Emulsion T-9

This example demonstrates a high aspect ratio (100) tabular emulsion where 1 mole percent iodide is present in the initial grain population and 50 mole percent bromide, is added during growth to make the final emulsion 0.3 mole percent iodide, 36 mole percent bromide, and 63.7 mole percent chloride.

A 2030 mL solution containing 3.52 percent by weight low methionine gelatin, 0.0056 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 2.25.

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 60 mL/min each. This achieved grain nucleation.

The mixture was then held for 10 minutes, the temperature remaining at 40 ° C. Following the hold, a 0.5 M silver nitrate solution and a 0.25 M sodium chloride and 0.25 M sodium bromide solution were added simultaneously at 8 mL/min for 40 minutes with the pCl being maintained at 2.25 to form crystals with an initial iodide concentration of 2 mole percent, based on total silver.

The resulting emulsion was a tabular grain silver iodobromochloride emulsion containing 0.27 mole percent iodide and 36 mole percent bromide, based on silver, the remaining halide being chloride. Fifty percent of total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.4 µm and an average thickness of 0.032 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 12.8 and an average tabularity (ECD/t^2) of 432. The ratio of major face edge lengths of the selected tabular grains was 1.9. Seventy one 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 0.38 µm, a mean thickness of 0.034 µm, a mean aspect ratio of 11.3 and a mean tabularity of 363.

Example 11 - Preparation of Tabular Silver Iodochloride Emulsion T-10

This example demonstrates the preparation of an emulsion, employing phthalated gelatin as a peptizer, that satisfies the requirements of the invention.

To a stirred reaction vessel containing a 310 mL solution that is 1.0 percent by weight phthalated gelatin, 0.0063 M sodium chloride and 3.1 X 10^{-4} M KI at 40 ° C, 6.0 mL of a 0.1 M silver nitrate aqueous solution and 6.0 mL of a 0.11 M sodium chloride solution were each added concurrently at a rate of 6 mL/min.

The mixture was then held for 10 minutes, the temperature remaining at 40 ° C. Following the hold, the silver and salt solutions were added simultaneously with a linearly accelerated flow from 3.0 mL/min to 9.0 mL/min over 15 minutes with the pCl of the mixture being maintained at 2.7.

The resulting emulsion was a high aspect ratio tabular grain silver iodochloride emulsion. Fifty percent of total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.37 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 10 and an average tabularity (ECD/t^2) of 330. Seventy 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 0.3 µm, a mean thickness of 0.04 µm, and a mean tabularity of 210.

Electron diffraction examination of the square and rectangular surfaces of the tabular grains confirmed major face {100} crystallographic orientation.

Example 12 - Preparation of Tabular Silver Iodochloride Emulsion T-11

This example demonstrates the preparation of an emulsion, employing an unmodified bone gelatin as a peptizer, that satisfies the requirements of the invention.

To a stirred reaction vessel containing a 2910 mL solution that is 0.69 percent by weight bone gelatin, 0.0056 M sodium chloride, 1.86 x 10^{-4} M KI and at 55 ° C and pH 6.5, 60 mL of a 4.0 M silver nitrate solution and 60.0 mL of a 4.0 M silver chloride solution were each added concurrently at a rate of 120 mL/min.

The mixture was then held for 5 minutes during which a 5000 mL solution that is 16.6 g/L of low methionine gelatin was added and the pH was adjusted to 6.5 and the pCl to 2.25. Following the hold, the silver and salt solutions were added simultaneously with a linearly accelerated flow from 10 mL/min to 25.8 mL/min over 63 minutes, the pCl of the mixture being maintained at 2.25.

The resulting emulsion was a high aspect ratio tabular grain silver iodochloride emulsion containing 0.01 mole percent iodide. About 65 percent of the total projected grain area was provided by tabular grains having an average ECD of 1.5 µm and an average thickness of 0.18 µm.

Example 13 - Preparation of Tabular Silver Chloride Emulsion T-12

A stirred reaction vessel containing 400 mL of a solution which was 0.5 percent in bone gelatin, 6mM in 3-amino-1H-1,2,4-triazole, 0.040 M in NaCl, and 0.20 M in sodium acetate was adjusted to pH 6.1 at 55 °C. To this solution at 55 °C were added simultaneously 5.0 mL of 4 M $AgNO_3$ and 5.0 mL of 4 M NaCl at a rate of 5 mL/min each. The temperature of the mixture was then increased to 75 °C at a constant rate, which required 12 minutes. After holding at this temperature for 5 minutes, the pH was adjusted to 6.2 and held to within ±0.1 of this value; the flow of the $AgNO_3$ solution was resumed at 5 mL/min until 0.8 mole of silver had been added. The flow of the NaCl solution was also resumed at a rate needed to maintain a constant pAg of 6.64.

The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 65 percent of the projected area of the total grain population. This tabular grain population had a mean ECD of 1.95 µm and a mean thickness of 0.165 µm. The average aspect ratio and tabularity were 11.8 and 71.7, respectively.

Example 14 - Preparation of Tabular Silver Chloride Emulsion T-13

This emulsion was prepared similar to that of Example 13, except that the precipitation was stopped when 0.4 mole of Ag had been added.

The resulting emulsion consisted of tabular grain having {100} major faces which made up 65 percent of the projected area of the total grain population. This tabular grain population had a mean ECD of 1.28 µm and a mean thickness of 0.130 µm. The average aspect ratio and tabularity were 9.8 and 75.7, respectively.

Example 15 - Preparation of Tabular Silver Chloride Emulsion T-14

This example was prepared similar to that of Example 14, except that the pH of the reaction vessel was adjusted to 3.6 for the last 95 percent of the $AgNO_3$ addition.

The resulting emulsion consisted of {100} tabular grains making up 60 percent of the projected area of the total grain population. This tabular grain population had a mean ECD of 1.39 µm, and a mean thickness of 0.180 µm. The average aspect ratio and tabularity were 7.7 and 43.0, respectively.

Example 16 - Preparation of Tabular Silver Bromochloride Emulsion T-15

This emulsion was prepared similar to that of Example 14, except that the salt solution was 3.6 M in NaCl and 0.4 M in NaBr.

The resulting AgBrCl (10 percent Br) emulsion consisted of {100} tabular grain making up 52 percent of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.28 µm, and a mean thickness of 0.115 µm. The average aspect ratio and tabularity were 11.1 and 96.7, respectively.

Example 17 - Preparation of Tabular Silver Chloride Emulsion T-16

This emulsion was prepared similar to that of Example 13, except that 3,5-diamino-1,2,4-triazole (2.4 mmole) was used as the {100} tabular grain nucleating agent.

The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 45 percent of the projected area of the total grain population. This tabular grain population had a mean ECD of 1.54 µm and a mean thickness of 0.20 µm. The average aspect ratio and tabularity were 7.7 and 38.5, respectively.

Example 18 - Preparation of Tabular Silver Chloride Emulsion T-17

This emulsion was prepared in a manner similar to that of Example 13, except that imidazole (9.6 mmole) was used as the {100} tabular grain nucleating agent.

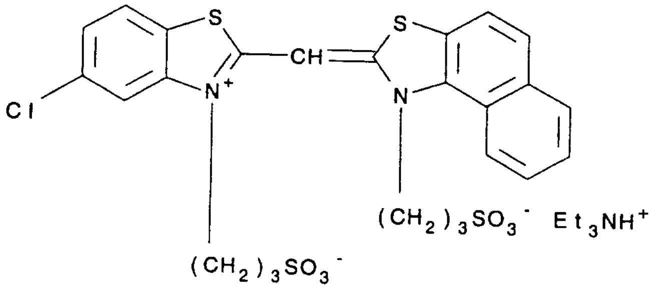
The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 40 percent of the projected area of the total grain population. This tabular grain population had a mean ECD of 2.20 µm and a mean thickness of 0.23 µm. The average aspect ratio and tabularity were 9.6 and 41.6, respectively.

Example 19 - Preparation of Tabular Silver Chloride Emulsion T-18

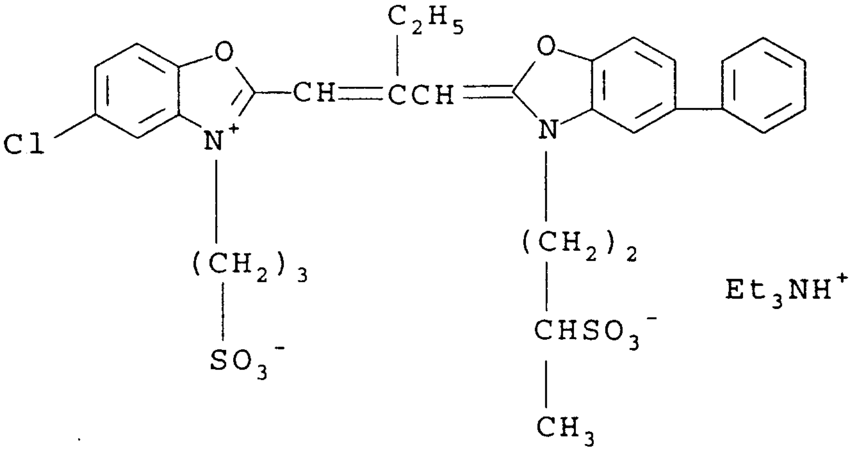
To a stirred reaction vessel containing 400 mL of a solution at 85C and pH 6.2 that was 0.25 weight percent in bone gelatin of low methionine content (<4 moles per gram of gelatin) and 0.008 M in NaCl were added simultaneously a 4 M $AgNO_3$ solution at 5.0 ml/min and a 4 M NaCl solution at a rate needed to maintain a constant pCl of 2.09. When 0.20 mole of $AgNO_3$ had been added, the additions were stopped for 20 seconds, during which time 15 ml of a 13.3 percent low methionine gelatin solution was added and the pH was adjusted to 6.2. The additions were resumed until a total of 0.4 mole of $AgNO_3$ had been added. The pH was held constant at 6.2 ± 0.1 during the precipitation.

The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 40 percent of the projected area of the total gain population. This tabular grain population had a mean equivalent circular diameter of 2.18 μm and a mean thickness of 0.199 μm. The average aspect ratio and tabularity were 11.0 and 55.0, respectively.

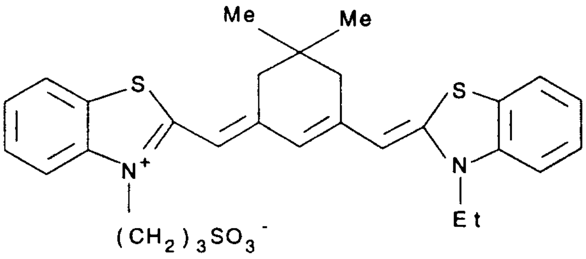
The sensitizing dyes and supersensitizing compound shown below are employed in the Examples to follow:



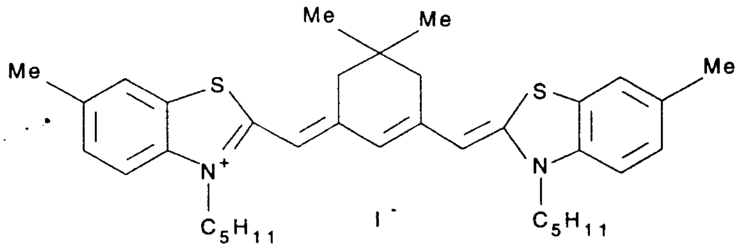
SS-52



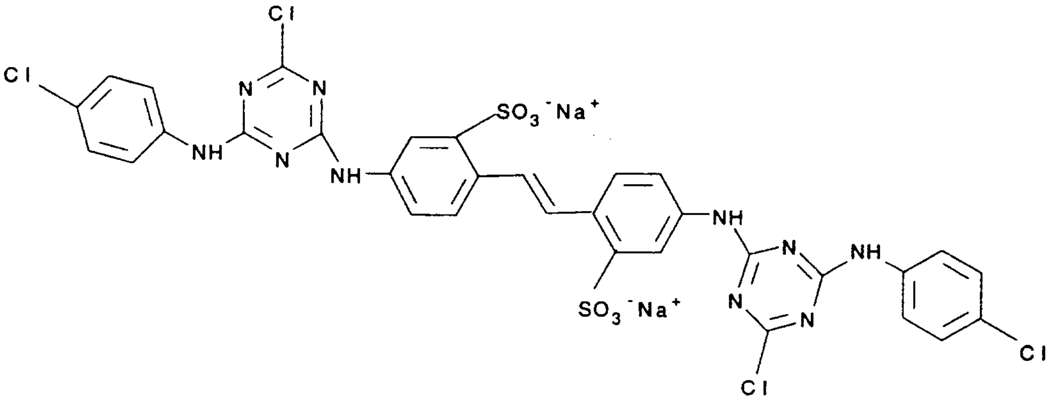
SS-53



SS-54



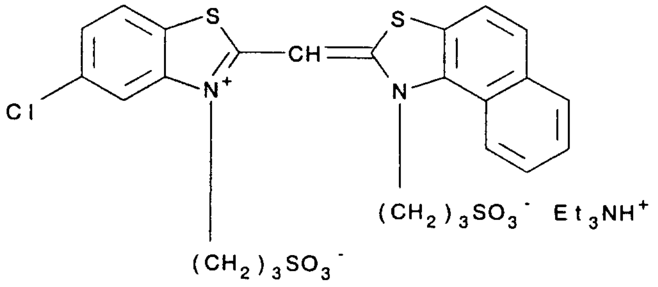
SS-55



SU-1

Example 20 - Preparation, Exposure, and Processing of Photographic Elements Containing Group A Stabilizer Compounds

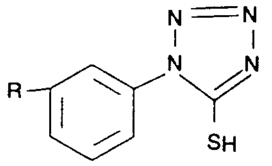
The tabular silver chloride emulsion T-1 of Example 2 was blue-sensitized as follows: 624 mg/silver mole of sensitizing dye SS-52 was added to the emulsion.



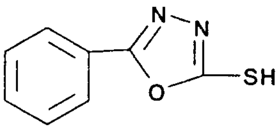
SS-52

After holding for 20 minutes, 2.4 mg/silver mole of colloidal gold sulfide was added. The mixture was heated to 60 °C, held at this temperature for 40 minutes, and then cooled to 40 °C. At this point, a mercapto-substituted heterocyclic photographic stabilizer compound of Group A was added to the emulsion. These stabilizer compounds are shown in Table 1.

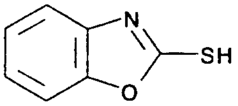
Table 1



	R
A-1	CH_3CONH
A-2	H
A-3	CH_3O
A-4	H_2NCONH
A-5	$HOOCCH_2NHCONH$
A-6	$C_2H_5OOCCONH$

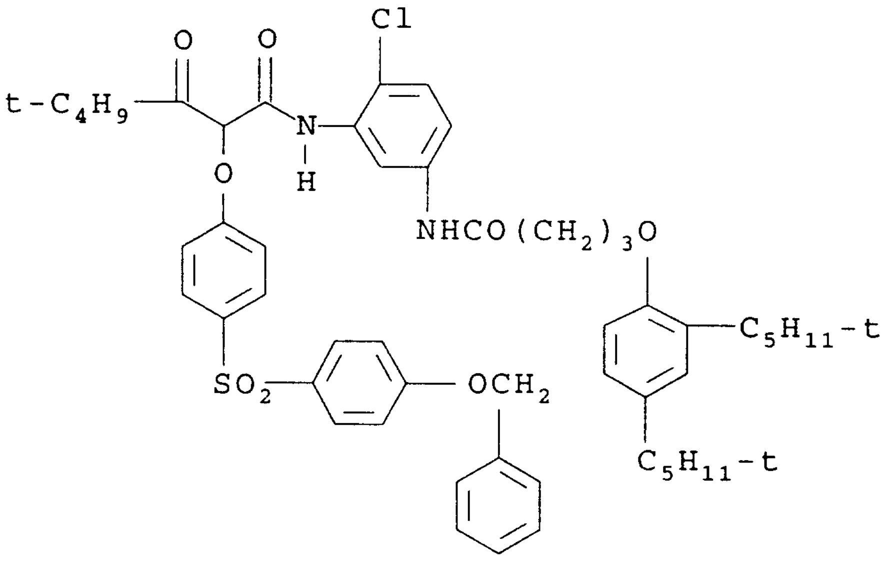


A-7



A-8

A dispersion of the yellow dye-forming coupler C-25 in dibutyl phthalate (4:1 weight ratio) was added to each of the emulsions, which were then coated on a resincoated paper support to form elements containing 0.34 g/m^2 of silver, 1.08 g/m^2 of coupler, and 1.51 g/m^2 of gelatin. A protective overcoat containing 1.076 g/m^2 of gelatin was applied, along with the hardener bis(vinylsulfonylmethyl) ether in an amount 1.8 weight percent of total gelatin.



C-25

The elements were given a 0.1 second exposure, using a 0-3 step tablet (0.15 increments) with a tungsten lamp having a color temperature of 3000K, log lux 2.95. The elements were exposed through a combination of magenta and yellow filters, 0.3 ND (Neutral Density) filter, and UV filter, designed to simulate a color negative print exposure source. The processing consisted of a color development (45 sec, 35 ° C), bleach-fix (45 sec, 35 ° C) and stabilization or water wash (90 sec, 35 ° C) followed by drying (60 sec, 60 ° C). The following solutions were used:

Developer

Lithium salt of sulfonated polystyrene	0.25 mL
Triethanolamine	11.0 mL
N,N-diethylhydroxylamine (85% by wt.)	6.0 mL
Potassium sulfite (45% by wt.)	0.5 mL
Color developing agent (4-(N-ethyl-N-2-methanesulfonylaminoethyl)-2-methyl-phenylenediamine sesquisulfate monohydrate	5.0 g
Stain reducing agent	2.3 g
Lithium sulfate	2.7 g
Potassium chloride	2.3 g
Potassium bromide	0.025 g
Sequestering agent	0.8 mL
Potassium carbonate	25.0 g
Water to total of 1 liter, pH adjusted to 10.12	

Bleach-fix

Ammonium sulfite	58 g
Sodium thiosulfate	8.7 g
Ethylenediaminetetracetic acid ferric ammonium salt	40 g
Acetic acid	9.0 mL
Water to total 1 liter, pH adjusted to 6.2	

Stabilizer

Sodium citrate	1 g
Water to total of 1 liter, pH adjusted to 7.2	

The sensitivity of the emulsion was measured at 1.0 density units above Dmin. Changes in sensitivity were measured on individual samples of each element that were subjected, prior to processing, to 1 day incubation at 60°C (140°F) and 1 week incubation at 48.9°C (120°F), relative to samples that were maintained at -17.8°C (0°F). Dmin increases, or fog, relative to the non-incubated samples were determined for the incubated samples of elements containing stabilizers and normalized with respect to the similarly determined fog values of the incubated control samples. The results of these measurements are collected in Table 2.

Table 2

Element	Stabilizer (mmole/ Agmole)	Keeping Conditions			
		1 day at 60°C		1 week at 37.8°C	
		sensitivity	normalized fog	sensitivity	normalized fog
1 control	none	*	100	*	100
2	A-1 (0.29)	29	33	36	41
3	A-1 (0.48)	22	25	25	35
4	A-2 (0.29)	34	36	41	44
5	A-2 (0.48)	32	39	39	44
6	A-3 (0.29)	31	33	37	40
7	A-3 (0.48)	26	25	29	34
8	A-4 (0.29)	28	25	33	35
9	A-4 (0.48)	20	21	25	29
10	A-5 (0.29)	42	49	54	53
11	A-5 (0.38)	34	39	43	49
12	A-6 (0.29)	29	36	35	42
13	A-6 (0.48)	23	29	28	35
14	A-7 (0.19)	65	25	70	37
15	A-7 (0.38)	46	9	45	15
16	A-8 (0.29)	59	54	88	63
17	A-8 (0.48)	43	40	52	50
* sensitivity could not be determined because of very high fog					

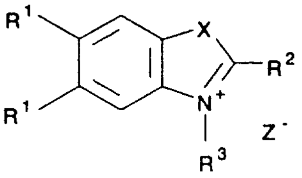
The results in Table 2 illustrate the substantial decreased changes in sensitivity and fog under accelerated keeping conditions that were provided by stabilizer compounds of Group A incorporated in the elements.

Example 21 - Preparation, Exposure, and Processing of Photographic Elements Containing Group B Stabilizer Compounds

Photographic elements were prepared, exposed, and processed as described in Example 20, except that quaternary aromatic chalcogenazolium salt photographic stabilizer compounds of Group B were included in the elements in place of the Group A compounds. Table 3 lists the Group B stabilizer compounds employed.

Table 3

Group B Stabilizer Compounds



	R1	X	Z⁻	R2	R3
B-1	H	Se	BF_4^-	CH_3	C_2H_5
B-2	H	S	BF_4^-	H	$CH_2CH_2CONHSO_2CH_3$
B-3	H	S	BF_4^-	H	$(CH_2)_{10}$-3-benzothiazolyl
B-4	H	S	BF_4^-	H	CH_3
B-5	H	S	BF_4^-	H	$CH_2=CHCH_2$
B-6	CH_3O	S	--	H	$CH_2CH_2CH_2SO_3^-$

Sensitivity changes and fog increases resulting from pre-processing incubation of the elements were determined as described in Example 20, except that the 1-week test was carried out at a temperature of 37.8 °C (100 °F) rather than 48.9 °C (120 °F). The results are shown in Table 4.

Table 4

Element	Stabilizer (mmole/Agmole)	Keeping conditions			
		1 day at 60 °C		1 week at 37.8 °C	
		sensitivity	normalized fog	sensitivity	normalized fog
1 control	none	46	100	24	100
2	B-1 (0.29)	25	58	13	55
3	B-1 (0.48)	16	44	8	45
4	B-2 (0.29)	18	58	12	80
5	B-2 (0.38)	19	64	13	85
6	B-3 (0.29)	22	78	8	90
7	B-3 (0.38)	19	64	8	75
8	B-4 (0.38)	39	78	21	60
9	B-5 (0.29)	18	56	9	70
10	B-5 (0.48)	15	62	7	80
11	B-6 (0.29)	32	86	15	70

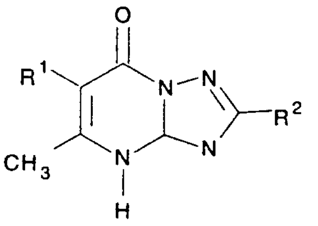
The results in Table 4 show that the changes in sensitivity and fog that resulted from accelerated keeping conditions were substantially diminished by the inclusion of Group B stabilizer compounds in the elements.

Example 22 - Preparation, Exposure, and Processing of Photographic Elements Containing Group C Stabilizer Compounds

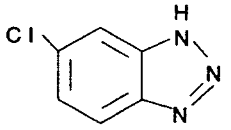
Photographic elements were prepared, exposed, and processed as described in Example 20, except that photographic stabilizers of Group C, heterocyclic compounds which contain an ionizable or dissociable hydrogen attached to a ring nitrogen atom, were included in the elements in place of Group A compounds. The Group C stabilizer compounds employed are listed in Table 5.

Table 5

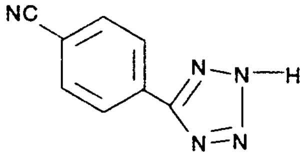
Group C Stabilizer Compounds



	R^1	R^2
C-1	H	H
C-2	Br	H
C-3	H	SCH_3
C-4	Br	SC_8H_{17}



C-5



C-6

Changes in sensitivity and fog arising from pre-processing incubation of the elements were determined as described in Example 21. Table 6 contains the results of these measurements.

Table 6

Element	Stabilizer (mmole/Agmole)	Keeping Conditions			
		1 day at 60 ° C		1 week at 37.8 ° C	
		sensitivity	normalized fog	sensitivity	normalized fog
1 control	none	50	100	25	100
2	C-1 (3.8)	23	46	16	50
3	C-1 (15.2)	17	46	12	67
4	C-2 (3.8)	19	25	6	21
5	C-2 (15.2)	19	40	7	50
6	C-3 (0.38)	21	46	16	46
7	C-3 (3.8)	19	73	12	96
8	C-4 (0.38)	20	48	10	63
9	C-4 (3.8)	16	50	14	54
10	C-5 (0.38)	31	35	16	33
11	C-5 (3.8)	23	46	9	42
12	C-6 (0.38)	29	58	19	63
13	C-6 (3.8)	26	58	14	63

As can be seen from the data in Table 6, inclusion of stabilizer compounds of Group C in the elements generally led to substantial lessening of sensitivity and fog changes arising from accelerated keeping conditions.

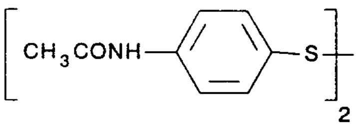
Example 23 - Preparation, Exposure and Processing of Photographic Elements Containing Other Stabilizer Compounds

Photographic elements were prepared, exposed, and processed as described in Example 20, except that other photographic stabilizers, identified in Tables 7 and 8 below, were included in the elements in place of the Group A compounds.

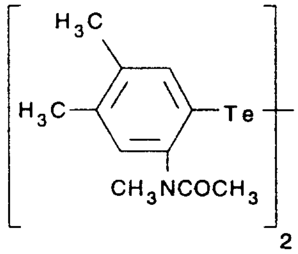
Table 7 contains the formulas of several dichalcogenide compounds that are representative photographic stabilizers of Group D.

Table 7

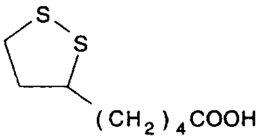
Group D Stabilizer Compounds



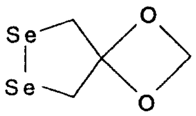
D-1



D-2



D-3



D-4

In addition to the compounds shown in Table 7, the following stabilizer compounds were included in individual photographic elements: mercuric chloride, benzoquinone, and a mixture of potassium benzenethiosulfonate and sodium p-toluenesulfinate.

Changes in sensitivity and fog resulting from pre-processing incubation of the elements were determined as described in Example 21. The results are given in Table 8.

Table 8

Element	Stabilizer (mmole/Agmole)	Keeping Conditions			
		1 day at 60 °C		1 week at 37.8 °C	
		sensitivity	normalized fog	sensitivity	normalized fog
1 control	none	68	100	21	100
2	D-1 (0.06)	6	20	8	30
3	D-2 (0.06)	6	22	5	35
4	D-3 (0.06)	27	58	7	60
5	D-4 (0.005)	18	17	9	25
6	$HgCl_2$ (0.037)	-11	18	-5	10
7	benzoquinone (0.37)	44	27	21	25
8	potassium tolylthiosulfonate (0.53) + sodium p-toluenesulfinate (0.67)	14	33	-1	15

The results in Table 8 demonstrate the substantially diminished changes in sensitivity and fog that resulted from preprocessing incubation of elements containing the various stabilizer compounds. In several instances, the incubation conditions appeared to cause slight sensitivity increases.

Example 24 - Preparation, Exposure, and Processing of Photographic Elements Containing 1-(3-Acetamidophenyl)-5-Mercaptotetrazole-Reducing Agent Mixtures

Photographic elements containing mixtures of 1-(3-acetamidophenyl)-5-mercaptotetrazole (stabilizer compound A-1 of Example 20) with various enolic reducing agents were prepared, exposed, and processed using the procedures described in Example 20. The enolic reducing agents employed were piperidinohexose reductone (PHR), catechol disulfonate (CDS), hydroquinone (HQ), and 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone (MOP). The amount of 1-(3-acetamidophenyl)-5-mercaptotetrazole included in each element was 0.38 mmole/Ag mole.

Dmin increases, or fog, were measured as described in Example 21 on samples of each element that were subjected, prior to processing, to 1 week incubation at 37.8C. These fog density values were normalized with respect to the fog observed for the incubated control sample. The results are summarized in Table 9.

Table 9

Element	Reducing agent (mmole/Agmole)	Keeping Condition 1 week at 37.8°C normalized fog
1	none	100
2	PHR (5.4)	13
3	CDS (33)	13
4	HQ (7)	19
5	MOP (3.6)	31

The data in Table 9 illustrate the substantial lessening of fog that resulted when enolic reducing agents typified by the compounds described above were included, along with stabilizer A-1, in photographic elements.

Claims

1. A radiation sensitive emulsion containing a silver halide grain population comprising at least 50 mole percent chloride, based on silver, characterized in that at least 50 percent of the grain population projected area is accounted for by tabular grains (a) bounded by {100} major faces having adjacent edge ratios of less than 10, and (b) each having an aspect ratio of at least 2, said emulsion comprising a photographic stabilizer that protects the emulsion against changes in sensitivity and fog upon aging and is:

A. A mercapto heterocyclic nitrogen compound containing a mercapto group bonded to a carbon atom which is linked to an adjacent nitrogen atom in a heterocyclic ring system,

B. A quaternary aromatic chalcogenazolium salt wherein the chalcogen is sulfur, selenium or tellurium,

C. A triazole or tetrazole containing an ionizable hydrogen bonded to a nitrogen atom in a heterocyclic ring system,

D. A dichalcogenide compound comprising an -X-X- linkage between carbon atoms wherein each X is divalent sulfur, selenium or tellurium,

E. An organic compound containing a thiosulfonyl group having the formula $-SO_2SM$ where M is a proton or cation,

F. A mercuric salt, or

G. A quinone compound.

2. A radiation sensitive emulsion according to claim 1 further characterized in that the photographic stabilizer is a mercapto heterocyclic nitrogen compound containing a mercapto group bonded to a carbon atom which is linked to an adjacent nitrogen atom in a heterocyclic ring.

3. A radiation sensitive emulsion according to claim 1 further characterized in that the photographic stabilizer is a quaternary aromatic chalcogenazolium salt wherein the chalcogen is sulfur, selenium or tellurium.

4. A radiation sensitive emulsion according to claim 1 further characterized in that the photographic stabilizer is a triazole or a tetrazole containing an ionizable hydrogen bonded to a nitrogen atom in a heterocyclic ring system.

5. A radiation sensitive emulsion according to claim 1 further characterized in that the stabilizer is a dichalcogenide compound comprising an -X-X- linkage between carbon atoms wherein each X is a divalent sulfur, selenium or tellurium.

6. A radiation sensitive emulsion according to any one of claims 1 to 5 inclusive further characterized in that an image dye-forming compound is located in reactive association with the emulsion.

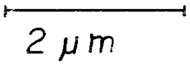
7. An emulsion according to any one of claims 1 to 6 inclusive further characterized in that the average aspect ratio is at least 5.

8. An emulsion according to claim 7 further characterized in that the average aspect ratio is greater than 8.

9. An emulsion according to any one of claims 1 to 8 inclusive further characterized in that the tabular grains have thicknesses of less than 0.3 µm.

10. An emulsion according to claim 9 further characterized in that the tabular grains have thicknesses of less than 0.2 µm.

FIG. 1



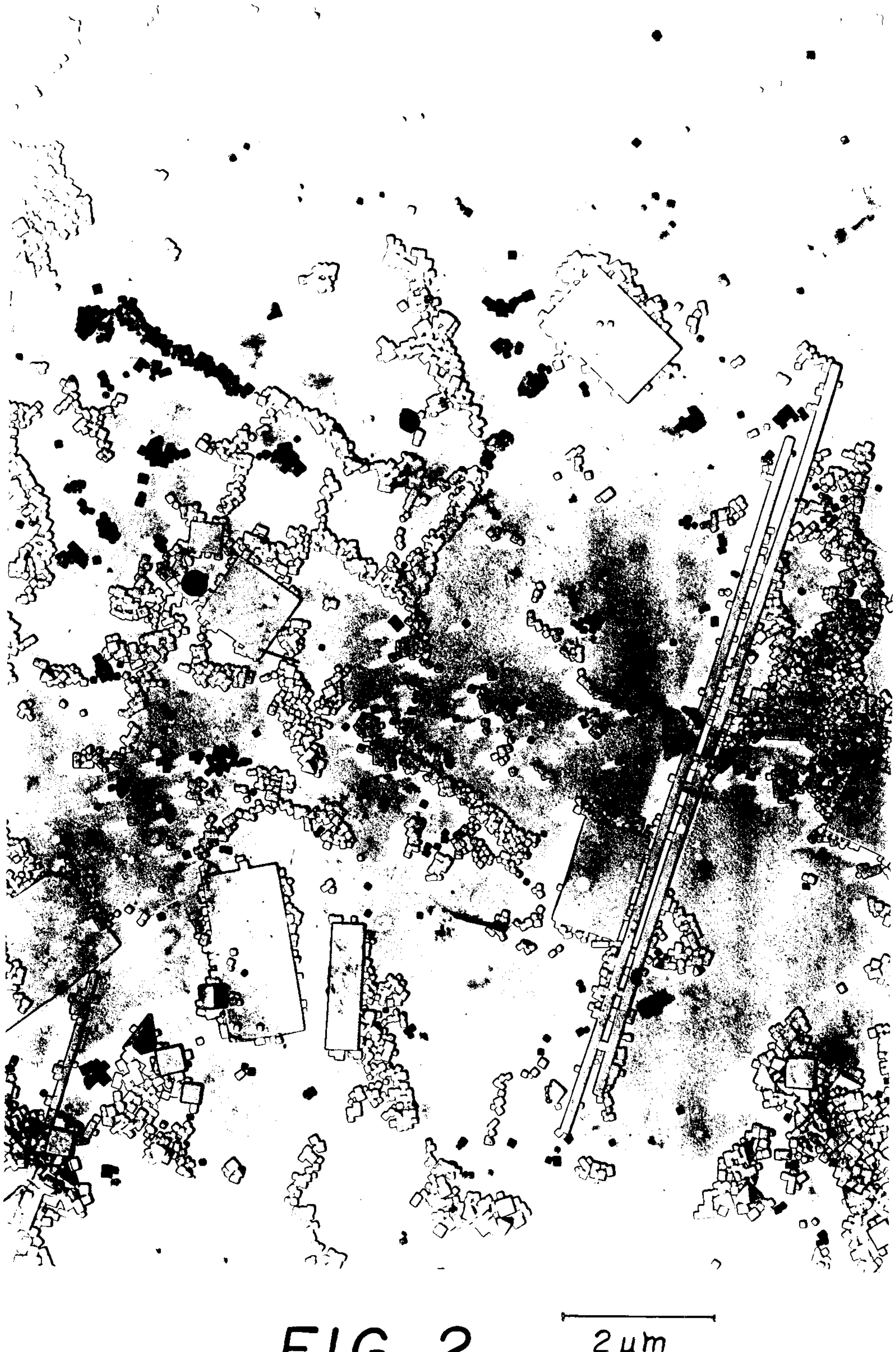


FIG. 2