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(54) Oligomer modified tabular grain emulsions.

(57) A radiation sensitive emulsion is disclosed comprised of a dispersing medium and silver halide grains. At least 50 percent of total grain projected area is accounted for by tabular grains bounded by {100} major faces having adjacent edge ratios of less than 10, each having an aspect ratio of at least 2, containing on average at least one pair of metal ions chosen from group VIII, periods 5 and 6, at adjacent cation sites in their crystal lattice, and internally at their nucleation site containing iodide and at least 50 mole percent chloride.

The emulsions are prepared by the steps of (a) introducing silver and halide salts into a dispersing medium so that nucleation of the tabular grains occurs in the presence of iodide with chloride accounting for at least 50 mole percent of the halide present in the dispersing medium and the pCl of the dispersing medium being maintained in the range of from 0.5 to 3.5, (b) following nucleation completing grain growth under conditions that maintain the {100} major faces of the tabular grains, and (c) during at least one of steps (a) and (b) introducing into the dispersing medium oligmers of group VIII, period 5 or 6, metal, wherein each oligomer contains at least two metal ions and on average at least two metal ions are incorporated in each grain in adjacent cation sites.

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FIG. 1

The invention relates to radiation sensitive silver halide emulsions and to processes for their preparation.

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, can 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 total grain 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 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} crystal-lographic 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.

Mignot U.S. Patent 4,386,156 represents an improvement over Bogg in that the disadvantages of ammoniacal ripening were avoided in preparing a silver bromide emulsion containing tabular grains with square and rectangular major faces. Mignot specifically requires ripening in the absence of silver halide ripening agents other than bromide ion (e.g., thiocyanate, thioether or ammonia).

Endo and Okaji, "An Empirical Rule to Modify the Habit of Silver Chloride to form Tabular Grains in an Emulsion", *The Journal of Photographic Science,* Vol. 36, pp. 182-188, 1988, discloses silver chloride emulsions prepared in the presence of a thiocyanate ripening agent. Emulsion preparations by the procedures disclosed has produced emulsions containing a few tabular grains within a general grain population exhibiting mixed {111} and {100} faces.

Mumaw and Haugh, "Silver Halide Precipitation Coalescence Processes", *Journal of Imaging Science*, Vol. 30, No. 5, Sept./Oct. 1986, pp. 198-299, is essentially cumulative with Endo and Okaji, with section IV-B being particularly pertinent.

Symposium: Torino 1963, *Photographic Science*, Edited by C. Semerano and U. Mazzucato, Focal Press, pp. 52-55, discloses the ripening of a cubic grain silver chloride emulsion for several hours at 77 °C. During ripening tabular grains emerged and the original cubic grains were depleted by Ostwald ripening. As demonstrated by the comparative Example below, after 3 hours of ripening tabular grains account for only a small fraction of the total grain projected area, and only a small fraction of the tabular grains were less than 0.3 μm in thickness. In further investigations going beyond the actual teachings provided, extended ripening eliminated many of the smaller cubic grains, but also degraded many of the tabular grains to thicker forms.

Japanese published patent application (Kokai) 02/024,643, laid open January 26, 1990, was cited in a Patent Cooperation Treaty search report as being pertinent to the tabular grain structures claimed, but is in Applicants' view unrelated. The claim is directed to a negative working emulsion containing a hydrazide derivative and tabular grains with an equivalent circular diameter of 0.6 to 0.2 μm. Only conventional tabular grain preparations are disclosed and only silver bromide and bromoiodide emulsions are exemplified.

Evans et al U.S. Patent 5,024,931 discloses a photographic silver halide emulsion comprised of radiation sensitive silver halide grains exhibiting a face centered cubic crystal lattice structure containing on average, at least one pair of metal ions chosen from group VIII, periods 5 and 6, at adjacent cation sites of the crystal lattice. Increased speed and reduced low intensity reciprocity failure are demonstrated in silver bromide emulsions.

In one aspect the invention is directed to a radiation sensitive emulsion containing a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population projected area, characterized in that at least 50 percent of total grain projected area is accounted for by tabular grains (1) bounded by {100} major faces having adjacent edge ratios of less than 10, (2) each having an aspect ratio of at least 2, and (3) containing on average at least one pair of metal ions chosen from group VIII, periods 5 and 6, at adjacent cation sites in their crystal lattice.

In another aspect this invention is directed to a process of preparing a radiation sensitive emulsion containing a dispersing medium and silver halide grains, characterized in that at least 50 percent of total grain projected area is accounted for by tabular grains (1) bounded by {100} major faces having adjacent edge ratios of less than 10, (2) each having an aspect ratio of at least 2, (3) containing on average at least one pair of metal ions chosen from group VIII, periods 5 and 6, at adjacent cation sites in their crystal

lattice, and (4) internally at their nucleation site containing iodide and at least 50 mole percent chloride are prepared by the steps comprised of (a) introducing silver and halide salts into a dispersing medium so that nucleation of the tabular grains occurs in the presence of iodide with chloride accounting for at least 50 mole percent of the halide present in the dispersing medium and the pCl of the dispersing medium being maintained in the range of from 0.5 to 3.5, (b) following nucleation completing grain growth under conditions that maintain the {100} major faces of the tabular grains, and (c) during at least one of steps (a) and (b) introducing into the dispersing medium oligomers of group VIII, period 5 or 6, metal, wherein each oligomer contains at least two metal ions and on average at least two metal ions are incorporated in each grain in adjacent cation sites.

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 present invention combines with the novel grain characteristics adjacent cation crystal lattice site grain dopants that are highly effective in improving photographic performance. Thus, not only does the invention represent the discovery of a novel process for preparing tabular grain emulsions, the emulsions that are produced by the process are novel. The invention places within the reach of the art tabular grains bounded by {100} crystal faces with halide contents, dopant contents and distributions and grain thicknesses that have not been heretofore realized. The present invention provides ultrathin tabular grain emulsion in which the grains are bounded by {100} crystal faces. The invention in a preferred form 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, the emulsions of the invention do not require a morphological stabilizer adsorbed to the major faces of the grains to maintain their tabular form. Finally, while clearly applicable 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 having the grain characteristics of the invention and

Figure 2 is a shadowed photomicrograph of carbon grain replicas of a control emulsion.

The photographically useful, radiation sensitive emulsions of the invention are comprised of a dispersing medium and silver halide grains. The emulsions contain a high chloride grain population. At least 50 percent of total grain projected area of the high chloride grain population is accounted for by tabular grains which (1) are bounded by {100} major faces having adjacent edge ratios of less than 10, (2) each have an aspect ratio of at least 2, and (3) contain on average at least one pair of metal ions chosen from group VIII, periods 5 and 6, at adjacent cation sites in the crystal lattice.

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

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

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

The grains remaining all have square or rectangular major faces, indicative of {100} crystal faces. To identify the tabular grains it is necessary to determine for each grain its ratio of ECD to thickness (t)--i.e., ECD/t. ECD is determined by measuring the projected area (the product of edge lengths) of the upper surface of each grain. From the grain projected area the ECD of the grain is calculated. Grain thickness is

commonly determined by oblique illumination of the grain population resulting in the individual grains casting shadows. From a knowledge of the shadow angle it is possible to calculate the thickness of a grain from a measurement of its shadow length. The grains having square or rectangular faces and each having a ratio of ECD/t of at least 2 are tabular grains having {100} major faces. When the projected areas of the {100} tabular grains account for at least 50 percent of total grain projected area, the emulsion is a tabular grain emulsion.

In the emulsion of Figure 1 tabular grains account for more than 50 percent of total grain projected area. From the definition of a tabular grain above, it is apparent that the average aspect ratio of the tabular grains can only approach 2 a minimum limit. In fact, tabular grain emulsions of the invention typically exhibit average aspect ratios of 5 or more, with high average aspect ratios (>8) being preferred. That is, preferred emulsions according to the invention are high aspect ratio tabular grain emulsions. In specifically preferred emulsions according to the invention average aspect ratios of the tabular grain population are at least 12 and optimally at least 20. Typically the average aspect ratio of the tabular grain population ranges up to 50, but higher aspect ratios of 100, 200 or more can be realized. Emulsions within the contemplation of the invention in which the average aspect ratio approaches the minimum average aspect ratio limit of 2 still provide a surface to volume ratio that is 200 percent that of cubic grains. The tabular grain population can exhibit any grain thickness that is compatible with the average aspect ratios noted above. However, particularly when the selected tabular grain population exhibits a high average aspect ratio, it is preferred to additionally limit the grains included in the selected tabular grain population to those that exhibit a thickness of less than 0.3 μm and, optimally, less than 0.2 μm. It is appreciated that the aspect ratio of a tabular grain can be limited either by limiting its equivalent circular diameter or increasing its thickness. Thus, when the average aspect ratio of the tabular grain population is in the range of from 2 to 8, the tabular grains accounting for at least 50 percent of total grain projected area can also each exhibit a grain thickness of less than 0.3 μm or less than 0.2 μm. Nevertheless, in the aspect ratio range of from 2 to 8 particularly, there are specific photographic applications that can benefit by greater tabular grain thicknesses. For example, in constructing a blue recording emulsion layer of maximum achievable speed it is specifically contemplated that tabular grain thicknesses that are on average 1 μm or even larger can be tolerated. This is because the eye is least sensitive to the blue record and hence higher levels of image granularity (noise) can be tolerated without objection. There is an additional incentive for employing larger grains in the blue record in that it is sometimes difficult to match in the blue record the highest speeds attainable in the green and red record. A source of this difficulty resides in the blue photon deficiency of sunlight. While sunlight on an energy basis exhibits equal parts of blue, green and red light, at shorter wavelengths the photons have higher energy. Hence on a photon distribution basis daylight is slightly blue deficient.

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

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

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

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

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

where

T is tabularity;

AR is aspect ratio;

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

t is grain thickness in micrometers.

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

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

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

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

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

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

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

The tabular grains described above accounting for at least 50 percent of total grain projected area and preferably all of the grains that are formed in the same precipitation contain on average at least one pair of metal ions chosen from group VIII, periods 5 and 6, at adjacent cation sites in their crystal lattice. Subsequent references to group VIII, periods 5 and 6, are also more succinctly designated group VIII 5/6.

The present invention is based on the discovery that, when adjacent cation positions of the face centered cubic crystal structure of the grains are occupied by group VIII 5/6 metal ions, they exhibit a disproportionately large effect on photographic performance as compared to that demonstrated by photographic emulsions in which the same group VIII 5/6 metal ions have been similarly introduced, but without any mechanism to achieve adjacent cation lattice placement. While a single pair, on average, of adjacent

group VIII 5/6 metal ions incorporated in the crystal lattice of the radiation sensitive grains of an emulsion is effective to enhance photographic performance, it is preferred to incorporate at least five pairs, on average, of adjacent group VIII 5/6 metal ions in the radiation sensitive grains, preferably at least ten pairs, on average. Average pair incorporations can be determined merely by dividing half the number of metal ions incorporated by the number of radiation sensitive silver halide grains present in the emulsion. The latter can be determined from a knowledge of mean grain size, grain shape, and the halide and silver content of the emulsion. The actual distribution of group VIII 5/6 metal ions within the grains can be expected to follow a Poisson error function distribution with the mean metal ion incorporation corresponding to the distribution mode.

The minimum group VIII 5/6 metal ion incorporations per grain satisfying the requirements of this invention are far below the minimum concentration levels of group VIII 5/6 metal ions taught to be effective by the art. For example, Smith and Trivelli U.S. Patent 2,448,060 discloses a minimum concentration of group VIII 5/6 metal coordination complex of 0.8 mg/100 grams of silver. When 100 group VIII 5/6 metal ions per grain are present in the emulsions of this invention, the coordination complex concentration in mg/100 grams of silver is still less than a 1/3 the minimum level taught to be effective by Smith and Trivelli. When emulsions with adjacent pairs of group VIII 5/6 metal ions are compared with conventional emulsions with random crystal lattice placements of group VIII 5/6 metal ions at concentrations ranging from minimums of 2, 10, or 20 group VIII 5/6 metal ions per grain up to 100 group VIII 5/6 metal ions per grain and higher, superior photographic enhancement by the emulsions satisfying the requirements of the invention are realized.

Once a sufficient number of adjacent pairs of group VIII 5/6 metal ions are incorporated into the grains to achieve maximum photographic efficiency, no useful purpose is realized by further increasing the presence of group VIII 5/6 metal ions. The present invention does not, however, prevent the inclusion of group VIII 5/6 metal ions, incorporated entirely or only partially as adjacent lattice position pairs, up to the maximum useful concentration levels taught in the art for group VIII 5/6 metal ion incorporation.

When group VIII metal ions from period 5 are incorporated at the concentration limit of Smith and Trivelli, less than approximately 40 mg/100 grams of silver, only elementary calculations are required to observe that there are only about 4 atoms of the period 5 group VIII metal per 10,000 atoms of silver. When the group VIII metal is chosen from period 6, this number is reduced by half to about 2 atoms per 10,000 atoms of silver. Smith and Trivelli set out as a preferred maximum less than approximately 20 mg/100 grams of silver, which amounts to only about 2 atoms of group VIII 5 metal or 1 atom of group VIII 6 metal per 10,000 atoms of silver. At the minimum level of 0.8 mg/100 grams of silver, only about 8 atoms of group VIII 5 metal or about 4 atoms of group VIII 6 metal per million silver atoms is present in the emulsions of Smith and Trivelli. Thus, adjacent cation lattice position placement of group VIII 5/6 metal ions can rarely, if ever, be achieved by employing hexacoordination complexes each containing a single group VIII 5/6 metal ion as taught by Smith and Trivelli.

It has been discovered that adjacent cation site placement of group VIII 5/6 metal ions in the face centered cubic lattice structure of silver halide grains can be achieved by introducing into the emulsion an oligomeric hexacoordination complex containing at least two group VIII 5/6 metal atoms. Although polymeric and oligomeric hexacoordination complexes are known having a higher number of group VIII 5/6 metal ions, those oligomers are preferred which contain up to about 20 group VIII 5/6 metal atoms. Specifically preferred are oligomers that contain about 6 to 10 group VIII 5/6 metal atoms.

The oligomeric coordination complexes contain two or more group VIII 5/6 metal atoms linked by bridging ligands. For comparison, consider the following compound:

(I) R_2MX_6

where

R represents hydrogen, alkali metal, or ammonium,

M represents a group VIII, period 5 or 6, metal (i.e., ruthenium, rhodium, palladium, osmium, iridium or platinum), and

X represents a halogen atom.

When the compound of formula (I) above is dissolved, it dissociates into an anionic hexacoordination complex satisfying the following formula:

(II) MX_6

wherein

M is a group VIII 5/6 atom and

X is a halide ligand.

The six halide ligands are positioned around the group VIII 5/6 metal atom in the same way that the halide ions are positioned around a single silver ion in the face centered crystal lattice structure of a silver halide grain. Imagining mutually perpendicular x, y and z axes intersecting at the group VIII 5/6 metal atom, two ligands lie along each of these three axes equally spaced from the group VIII 5/6 metal atom. A corresponding anionic hexacoordination complex containing two group VIII 5/6 metal atoms is represented by the following formula:

(III) M_2L_{10}

wherein

M is as previously defined and

L is a halide or other bridging ligand. The difference between this anionic dimer and two anions satisfying formula II is that in the dimer the metal atoms share two bridging ligands, reducing the number of ligands required from 12 to 10. For oligomeric complexes containing up to five metal atoms the following general formula can be written to describe the anions:

(IV) $M_mL_{6+4(m-1)}$

where M and L are as previously defined and m is from 2 to 5. When the number of group VIII 5/6 metal atoms reaches six, a ring structure becomes possible made up of six group VIII 5/6 metal atoms and pairs of shared bridging ligands linking adjacent metal atoms. Although rings having higher numbers of group VIII metal atoms are possible, most higher molecular weight oligomers consist of rings containing six group VIII 5/6 metal atoms, usually with a pair of metal atoms in one ring shared with a pair of metal atoms in an adjacent ring. The following are exemplary of oligomeric anions satisfying the requirements of the invention containing 6, 8 or 10 group VIII 5/6 metal atoms:

(V) M_6L_{24}

(VI) M_8L_{32}

(VII) $M_{10}L_{38}$

wherein M and L are as previously defined. Other oligomeric forms containing 6, 8 or 10 group VIII 5/6 metal atoms are, of course, possible.

The net negative charge of the anions above is not indicated, since this depends upon the choice of the group VIII 5/6 metal and the ligand; the more electronegative ligands tending to shift the group VIII 5/6 metal to a higher oxidation state and the differing group VIII 5/6 metals exhibiting differing oxidative state preferences. For anions containing iridium and halide ligands, the net negative charge of the anion in formula II is -2, in formula III -4, in formula V -6, and in formulae VI and VII -8. With anionic hexacoordination complexes having negative charges ranging from -2 to -8 all having been demonstrated to be effective, it is apparent that the magnitude of net negative charge has little, if any, influence on the desired lattice placements.

The important point to observe is that all of the molecular weight and sterically varied oligomers contemplated for use in the practice of this invention exhibit a pattern of alternating group VIII 5/6 atoms and ligands similar to that found in the face centered cubic crystal lattice structure of a radiation sensitive silver halide grain. Thus, the oligomers are capable of presenting the group VIII metal atoms of the oligomers to the surface of the crystal lattice structure as it is being formed so that adjacent group VIII 5/6 atoms are oriented to occupy adjacent cation sites of the crystal lattice structure. It is also possible to achieve adjacent incorporations of group VIII metal atoms employing oligomeric tetracoordination complexes in place of hexacoordination complexes.

The bridging ligands are capable of forming covalent bonds with two adjacent group VIII 5/6 metal atoms. In their simplest form the ligands can be halides, such as fluoride, chloride, bromide, or iodide atoms. For size compatibility with the face centered cubic crystal lattice structure of silver halide grains the ligands are preferably chloride or bromide ligands. Other bridging ligand choices in addition to halide ions are possible. For example, to a limited extent aquo (HOH) ligands can be substituted for halide ligands. Pseudohalogen ligands, such as cyanide (CN), cyanate (OCN), thiocyanate (SCN), selenocyanate (SeCN),

and tellurocyanate (TeCN) ligands are contemplated. Still other ligands, such as nitrosyl (NO), thionitrosyl (NS), azide (N_3), oxo (O), and carbonyl (CO) ligands are possible. In choosing ligands other than halide and aquo ligands it must be borne in mind that the ligands can themselves affect photographic performance. When the ligands are the same halide as that of the grain structure, modifying effects are entirely attributable to the group VIII 5/6 metal ions incorporated. Similarly, aquo ligands have not been reported to produce modifying effects.

The anionic hexacoordination complexes paired with one or more charge satisfying cations, such as any of those indicated above satisfying R in formula I, can be introduced as a particulate solid or in solution at any stage of emulsion preparation employing any convenient conventional technique for hexacoordination complex addition--e.g., as taught by Smith and Trivelli, cited above and here incorporated by reference. To insure incorporation of the group VIII 5/6 metal in the crystal structure it is preferred to have the hexacoordination complex present during grain formation. Having the complex present before or during silver halide precipitation is contemplated. Also the group VIII 5/6 metal can be effectively incorporated by having the complex present while surface ripening of the grains is occurring--i.e., having the complex and one or more ripening agents concurrently present in the emulsion. The concentrations of the group VIII 5/6 metals introduced into the grains are too low to exert any significant influence on the shape or distribution of the grains produced.

Obtaining emulsions satisfying the requirements of the invention has been achieved by the discovery of a novel precipitation process. In this process grain nucleation occurs in a high chloride environment in the presence of iodide ion under conditions that favor the emergence of {100} crystal faces. As grain formation occurs the inclusion of iodide into the cubic crystal lattice being formed by silver ions and the remaining halide ions is disruptive because of the much larger diameter of iodide ion as compared to chloride ion. The incorporated iodide ions introduce crystal irregularities that in the course of further grain growth result in tabular grains rather than regular (cubic) grains.

It is believed that at the outset of nucleation the incorporation of iodide ion into the crystal structure results in cubic grain nuclei being formed having one or more 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 the growth accelerating irregularities. However, when any two contiguous cubic crystal faces contain the 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 the 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 the preferred form of the invention silver iodochloride grain nuclei are formed during the nucleation step. Minor amounts of bromide ion can be present in the dispersing medium during nucleation. Any amount of bromide ion can be present in the dispersing medium during nucleation that is compatible with at least 50 mole percent of the halide in the grain nuclei being chloride ions. The grain nuclei preferably contain at least 70 mole percent and optimally at least 90 mole percent chloride ion, based on silver.

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

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

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

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

The peptizer can take any convenient conventional form known to be useful in the precipitation of photographic silver halide emulsions and particularly tabular grain silver halide emulsions. A summary of conventional peptizers is provided in *Research Disclosure,* Vol. 308, December 1989, Item 308119, Section IX. *Research Disclosure* is published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire P010 7DD, England. 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 above, 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 of this invention, 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 above.

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

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

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

If desired, the rate of ripening can be increased by the presence of a ripening agent in the emulsion during the holding period. A conventional simple approach to accelerating ripening is to increase the halide ion concentration in the dispersing medium. This creates complexes of silver ions with plural halide ions that accelerate ripening. When this approach is employed, it is preferred to increase the chloride ion concentration in the dispersing medium. That is, it is preferred to lower the pCl of the dispersing medium into a range in which increased silver chloride solubility is observed. Alternatively, ripening can be accelerated and the percentage of total grain projected area accounted for by {100} tabular grains can be increased by employing conventional ripening agents. Preferred ripening agents are sulfur containing ripening agents, such as thioethers and thiocyanates. Typical thiocyanate ripening agents are disclosed by Nietz et al U.S. Patent 2,222,264, Lowe et al U.S. Patent 2,448,534 and Illingsworth U.S. Patent 3,320,069, the disclosures of which are here incorporated by reference. Typical thioether ripening agents are disclosed by McBride U.S. Patent 3,271,157, Jones U.S. Patent 3,574,628 and Rosencrantz et al U.S. Patent 3,737,313, the disclosures of which are here incorporated by reference. More recently crown thioethers have been suggested for use as ripening agents. Ripening agents containing a primary or secondary amino moiety, such as imidazole, glycine or a substituted derivative, are also effective. Sodium sulfite has also been demonstrated to be effective in increasing the percentage of total grain projected accounted by the {100} tabular grains.

Once the desired population of grain nuclei have been formed, grain growth to obtain the emulsions of the invention can proceed according to any convenient conventional precipitation technique for the precipitation of silver halide grains bounded by {100} grain faces. Whereas iodide and chloride ions are required to be incorporated into the grains during nucleation and are therefore present in the completed grains at the internal nucleation site, any halide or combination of halides known to form a cubic crystal lattice structure can be employed during the growth step. Neither iodide nor chloride ions need be incorporated in the grains during the growth step, since the irregular grain nuclei faces that result in tabular

grain growth, once introduced, persist during subsequent grain growth independently of the halide being precipitated, provided the halide or halide combination is one that forms a cubic crystal lattice. This excludes only iodide levels above 13 mole percent (preferably 6 mole percent) in precipitating silver iodochloride, levels of iodide above 40 mole percent (preferably 30 mole percent) in precipitating silver iodobromide, and proportionally intermediate levels of iodide in precipitating silver iodohalides containing bromide and chloride. When silver bromide or silver iodobromide is being deposited during the growth step, it is preferred to maintain a pBr within the dispersing medium in the range of from 1.0 to 4.2, preferably 1.6 to 3.4. When silver chloride, silver iodochloride, silver bromochloride or silver iodobromochloride is being deposited during the growth step, it is preferred to maintain the pCl within the dispersing medium within the ranges noted above in describing the nucleation step.

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

During the growth step both silver and halide salts are preferably introduced into the dispersing medium. In other words, double jet precipitation is contemplated, with added iodide salt, if any, being introduced with the remaining halide salt or through an independent jet. The rate at which silver and halide salts are introduced is controlled to avoid renucleation--that is, the formation of a new grain population. Addition rate control to avoid renucleation is generally well known in the art, as illustrated by Wilgus German OLS No. 2,107,118, Irie U.S. Patent 3,650,757, Kurz U.S. Patent 3,672,900, Saito U.S. Patent 4,242,445, Teitschied et al European Patent Application 80102242, and Wey "growth Mechanism of AgBr Crystals in Gelatin Solution", *Photographic Science and Engineering*, Vol. 21, No. 1, Jan./Feb. 1977, p. 14, *et seq*.

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

It is herein contemplated that various parameters important to the control of grain formation and growth, such as pH, pAg, ripening, temperature, and residence time, can be independently controlled in the separate nucleation and growth reaction vessels. To allow grain nucleation to be entirely independent of grain growth occurring in the growth reaction vessel down stream of the nucleation reaction vessel, no portion of the contents of the growth reaction vessel should be recirculated to the nucleation reaction vessel. Preferred arrangements that separate grain nucleation from the contents of the growth reaction vessel are disclosed by Mignot U.S. Patent 4,334,012 (which also discloses the useful feature of ultrafiltration during grain growth), Urabe U.S. Patent 4,879,208 and published European Patent Applications 326,852, 326,853, 355,535 and 370,116, Ichizo published European Patent Application 0 368 275, Urabe et al published European Patent Application 0 374 954, and Onishi et al published Japanese Patent Application (Kokai) 172,817-A (1990).

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

It has been observed that rapid grain nucleations, including so-called dump nucleations, in which significant levels of dispersing medium supersaturation with halide and silver ions exist at nucleation

accelerate introduction of the grain irregularities responsible for tabularity. Since nucleation can be achieved essentially instantaneously, immediate departures from initial supersaturation to the preferred pCl ranges noted above are entirely consistent with this approach.

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

The emulsions of the invention include silver chloride, silver iodochloride emulsions, silver iodobromochloride emulsions and silver iodochloro-bromide emulsions. Conventional grain dopants (other than group VIII metal 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. For example, compounds of metals such as copper, thallium, lead, mercury, bismuth, zinc, cadmium and rhenium can be present during grain precipitation, preferably during the growth stage of precipitation. Conventional grain dopant selections are illustrated by *Research Disclosure*, Vol. 308, Dec. 1989, Item 308,119, Section I, subsection D.

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

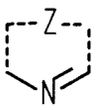
Although not essential to the practice of the invention, a further procedure that can be employed to maximize the population of tabular grains having {100} major faces is to incorporate an agent capable of restraining the emergence of non-{100} grain crystal faces in the emulsion during its preparation.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

Useful restraining agents under the contemplated conditions of precipitation are organic compounds containing a nitrogen atom with a resonance stabilized π 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 π electron pair of the nitrogen atom. The nitrogen atom can either be incorporated in an aromatic ring, such as an azole or azine ring, or the nitrogen atom can be a ring substituent of an aromatic ring.

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

(I)

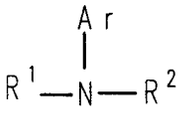


where

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

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

(II)



where

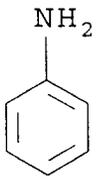
Ar is an aromatic ring structure containing from 5 to 14 carbon atoms and

R^1 and R^2 are independently hydrogen, Ar, or any convenient aliphatic group or together complete a five or six membered ring.

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

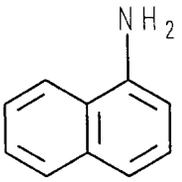
The following are representative of compounds contemplated satisfying formulae I and/or II:

R-1



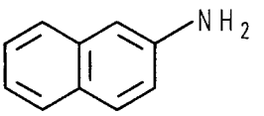
aniline

RA-2



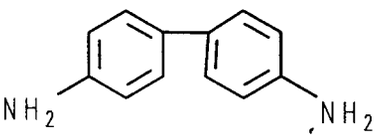
α-naphthylamine

RA-3



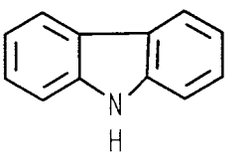
β-naphthylamine

RA-4



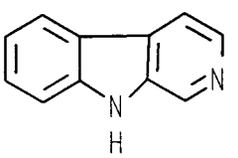
benzidine

RA-5



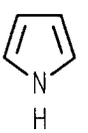
carbazole

RA-6



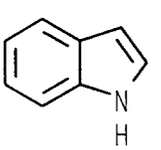
norharman

RA-7



pyrrole

RA-8



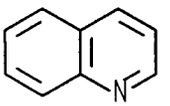
indole

RA-9



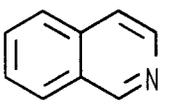
pyridine

RA-10



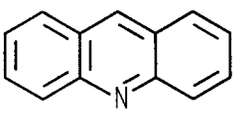
quinoline

RA-11



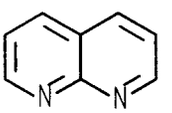
isoquinoline

RA-12



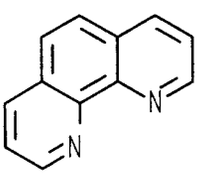
acridine

RA-13



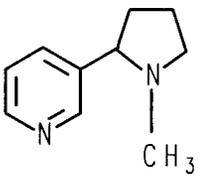
1,8-naphthyridine

RA-14



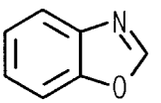
1,10-phenanthroline

RA-15



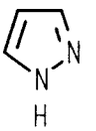
nicotine

RA-16



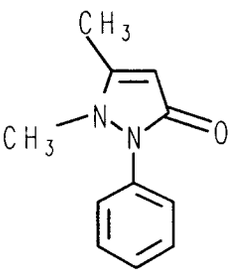
benzoxazole

RA-17



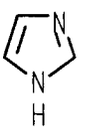
pyrazole

RA-18



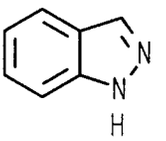
antipyrine

RA-19



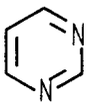
imidazole

RA-20



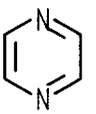
indazole

RA-21



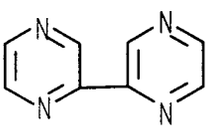
pyrimidine

RA-22



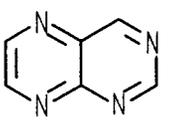
pyrazine

RA-23



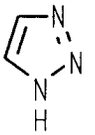
2,2'-bipyrazine

RA-24



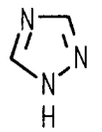
pteridine

RA-25



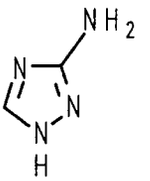
1,2,3-triazole

RA-26



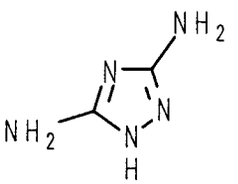
1,2,4-triazole

RA-27



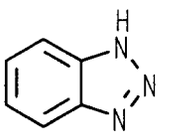
3-amino-1,2,4-triazole

RA-28



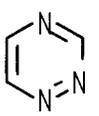
3,5-diamino-1,2,4-triazole

RA-29



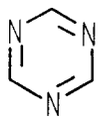
benzotriazole

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 the 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, such as at pAg levels of from 5 to 10, pH levels of from 5 to 8 and temperatures of from 30 to 80 °C, as illustrated by *Research Disclosure*, Vol. I20, April, 1974, Item I2008, *Research Disclosure*, Vol. I34, June, 1975, Item I3452, Sheppard et al U.S. Patent I,623,499, Matthies et al U.S. Patent I,673,522, Waller et al U.S. Patent 2,399,083, Damschroder et al U.S. Patent 2,642,36I, 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 3,772,03I, Gilman et al U.S. Patent 3,76I,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 3,904,4I5 and Simons U.K. Patent 1,396,696; chemical sensitization being optionally conducted in the presence of thiocyanate derivatives as described in Damschroder U.S. Patent 2,642,36I; thioether compounds as disclosed in Lowe et al U.S. Patent 2,52I,926, Williams et al U.S. Patent 3,021,215 and Bigelow U.S. Patent 4,054,457; and azaindenes, azapyridazines and azapyrimidines as described in Dostes U.S. Patent 3,411,914, Kuwabara et al U.S. Patent 3,554,757, Oguchi et al U.S. Patent 3,565,63I 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 3,89I,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. I36, August, 1975, Item I3654, Lowe et al U.S. Patents 2,5I8,698 and 2,739,060, Roberts et al U.S. Patents 2,743,I82 and 'I83, Chambers et al U.S. Patent 3,026,203 and Bigelow et al U.S. Patent 3,36I,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 of 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. 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 3,50l,3l0, 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 sensitizing dyes for sensitizing the emulsions of the invention 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, 2,9l7,5l6, 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-sulfobuyl)-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-carboxyethyl)-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-isoxazolin-5-one
SS-34
5-(3-Ethylbenzoxazolin-2-ylidene)-3-phenylrhodanine
SS-35
1,3-Diethyl-5-{[1-ethyl-3-(3-sulfopropyl)benzimidazolin-2-ylidene]ethylidene)-2-thiobarbituric acid
SS-36
5-[2-(3-Ethylbenzoxazolin-2-ylidene)ethylidene]-1-methyl-2-dimethylamino-4-oxo-3-phenylimidazol-inium *p*-toluenesulfonate
SS-37
5-[2-(5-Carboxy-3-methylbenzoxazolin-2-ylidene)ethylidene]-3-cyano-4-phenyl-1-(4-methylsulfonamido-3-pyrrolin-5-one
SS-38
2-[4-(Hexylsulfonamido)benzoylcyanomethine]-2-*{*2-{3-(2-methoxyethyl)-5-[(2-methoxyethyl)sulfonamido]-benzoxazolin-2-ylidene)ethylidene*}*acetonitrile
SS-39
3-Methyl-4-[2-(3-ethyl-5,6-dimethylbenzotellurazolin-2-ylidene)ethylidene]-1-phenyl-2-pyrazolin-5-one
SS-40
3-Heptyl-1-phenyl-5-{4-[3-(3-sulfobutyl)-naphtho[1,2-d]thiazolin]-2-butenylidene}-2-thiohydantoin
SS-41
1,4-Phenylene-bis(2-aminovinyl-3-methyl-2-thiazolinium] dichloride

SS-42
Anhydro-4-{2-[3-(3-sulfopropyl)thiazolin-2-ylidene]ethylidene}-2-{3-[3-(3-sulfopropyl)thiazolin-2-ylidene]-propenyl-5-oxazolium, hydroxide, sodium salt
SS-43
3-Carboxymethyl-5-{3-carboxymethyl-4-oxo-5-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-thiobar-bituric 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

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

To avoid such instability in emulsion coatings, stabilizers and antifoggants can be employed, such as halide ions (e.g., bromide salts); chloropalladates and chloropalladites as illustrated by Trivelli et al U.S. Patent 2,566,263; water-soluble inorganic salts of magnesium, calcium, cadmium, cobalt, manganese and zinc as illustrated by Jones U.S. Patent 2,839,405 and Sidebotham U.S. Patent 3,488,709; mercury salts as illustrated by Allen et al U.S. Patent 2,728,663; selenols and diselenides as illustrated by Brown et al U.K. Patent l,336,570 and Pollet et al U.K. Patent l,282,303; quaternary ammonium salts of the type illustrated by Allen et al U.S. Patent 2,694,7l6, Brooker et al U.S. Patent 2,131,038, Graham U.S. Patent 3,342,596 and Arai et al U.S. Patent 3,954,478; azomethine desensitizing dyes as illustrated by Thiers et al U.S. Patent 3,630,744; isothiourea derivatives as illustrated by Herz et al U.S. Patent 3,220,839 and Knott et al U.S. Patent 2,5l4,650; thiazolidines as illustrated by Scavron U.S. Patent 3,565,625; peptide derivatives as illustrated by Maffet U.S. Patent 3,274,002; pyrimidines and 3-pyrazolidones as illustrated by Welsh U.S. Patent 3,161,515 and Hood et al U.S. Patent 2,75l,297; azotriazoles and azotetrazoles as illustrated by Baldassarri et al U.S. Patent 3,925,086; azaindenes, particularly tetraazaindenes, as illustrated by Heimbach U.S. Patent 2,444,605, Knott U.S. Patent 2,933,388, Williams U.S. Patent 3,202,5l2, *Research Disclosure*, Vol. l34, June, 1975, Item l3452, and Vol. l48, August, 1976, Item 14851, and Nepker et al U.K. Patent l,338,567; mercaptotetrazoles, -triazoles and -diazoles as illustrated by Kendall et al U.S. Patent 2,403,927, Kennard et al U.S. Patent 3,266,897, *Research Disclosure*, Vol. 116, December, 1973, Item 11684, Luckey et al U.S. Patent 3,397,987 and Salesin U.S. Patent 3,708,303; azoles as illustrated by Peterson et al U.S. Patent 2,27l,229 and *Research Disclosure*, Item 11684, cited above; purines as illustrated by Sheppard et al U.S. Patent 2,319,090, Birr et al U.S. Patent 2,l52,460, *Research Disclosure*, Item l3452, cited above, and Dostes et al French Patent 2,296,204, polymers of l,3-dihydroxy(and/or l,3-carbamoxy)-2-methylenepropane as illustrated by Saleck et al U.S. Patent 3,926,635 and tellurazoles, tellurazolines, tellurazolinium salts and tellurazolium salts as illustrated by Gunther et al U.S. Patent 4,661,438, aromatic oxatellurazinium salts as illustrated by Gunther, U.S. Patent 4,581,330 and Przyklek-Elling et al U.S. Patents 4,661,438 and 4,677,202. High-chloride emulsions can be stabilized by the presence, especially during chemical sensitization, of elemental sulfur as described by Miyoshi et al European published Patent Application EP 294,149 and Tanaka et al European published Patent Application EP 297,804 and thiosul-

fonates as described by Nishikawa et al European published Patent Application EP 293,917.

Among useful stabilizers for gold sensitized emulsions are water-insoluble gold compounds of benzothiazole, benzoxazole, naphthothiazole and certain merocyanine and cyanine dyes, as illustrated by Yutzy et al U.S. Patent 2,597,9l5, and sulfinamides, as illustrated by Nishio et al U.S. Patent 3,498,792.

Among useful stabilizers in layers containing poly(alkylene oxides) are tetraazaindenes, particularly in combination with Group VIII noble metals or resorcinol derivatives, as illustrated by Carroll et al U.S. Patent 2,7l6,062, U.K. Patent l,466,024 and Habu et al U.S. Patent 3,929,486; quaternary ammonium salts of the type illustrated by Piper U.S. Patent 2,886,437; water-insoluble hydroxides as illustrated by Maffet U.S. Patent 2,953,455; phenols as illustrated by Smith U.S. Patents 2,955,037 and '038; ethylene diurea as illustrated by Dersch U.S. Patent 3,582,346; barbituric acid derivatives as illustrated by Wood U.S. Patent 3,6l7,290; boranes as illustrated by Bigelow U.S. Patent 3,725,078; 3-pyrazolidinones as illustrated by Wood U.K. Patent 1,158,059 and aldoximines, amides, anilides and esters as illustrated by Butler et al U.K. Patent 988,052.

The emulsions 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.

Among stabilizers useful in protecting the emulsion layers against dichroic fog are addenda such as salts of nitron as illustrated by Barbier et al U.S. Patents 3,679,424 and 3,820,998; mercaptocarboxylic acids as illustrated by Willems et al U.S. Patent 3,600,l78; and addenda listed by E. J. Birr, *Stabilization of Photographic Silver Halide Emulsions*, Focal Press, London, 1974, pp. l26-2l8.

Among stabilizers useful in protecting emulsion layers against development fog are addenda such as azabenzimidazoles as illustrated by Bloom et al U.K. Patent 1,356,142 and U.S. Patent 3,575,699, Rogers U.S. Patent 3,473,924 and Carlson et al U.S. Patent 3,649,267; substituted benzimidazoles, benzothiazoles, benzotriazoles and the like as illustrated by Brooker et al U.S. Patent 2,131,038, Land U.S. Patent 2,704,72l, Rogers et al U.S. Patent 3,265,498; mercapto-substituted compounds, e.g., mercaptotetrazoles, as illustrated by Dimsdale et al U.S. Patent 2,432,864, Rauch et al U.S. Patent 3,081,170, Weyerts et al U.S. Patent 3,260,597, Grasshoff et al U.S. Patent 3,674,478 and Arond U.S. Patent 3,706,557; isothiourea derivatives as illustrated by Herz et al U.S. Patent 3,220,839, and thiodiazole derivatives as illustrated by von Konig U.S. Patent 3,364,028 and von Konig et al U.K. Patent 1,186,441.

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, and mucohalogenic acids in combination with urazoles as illustrated by Allen et al U.S. Patents 3,232,76l and 3,232,764, or further in combination with maleic acid hydrazide as illustrated by Rees et al U.S. Patent 3,295,980.

To protect emulsion layers coated on linear polyester supports, addenda can be employed such as parabanic acid, hydantoin acid hydrazides and urazoles as illustrated by Anderson et al U.S. Patent 3,287,l35, and piazines containing two symmetrically fused 6-member carbocyclic rings, especially in combination with an aldehyde-type hardening agent, as illustrated in Rees et al U.S. Patent 3,396,023.

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; azole and mercaptotetrazole hydrophilic colloid dispersions of the type disclosed by *Research Disclosure*, Vol. 116, December, 1973, Item 11684; plasticized gelatin compositions of the type disclosed by Milton et al U.S. Patent 3,033,680; water-soluble interpolymers of the type disclosed by Rees et al U.S. Patent 3,536,49l; 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 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, Salesin U.S. Patent 3,708,303, 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 3,386,83l; alkenyl benzothiazolium salts as illustrated by Arai et al U.S. Patent 3,954,478; hydroxy-substituted benzylidene derivatives as illustrated by Thurston U.K. Patent l,308,777 and Ezekiel et al U.K. Patents l,347,544 and l,353,527; mercapto-substituted compounds of the type disclosed by Sutherns U.S. Patent 3,519,427; metal-organic complexes of the type disclosed by Matejec et al U.S. Patent 3,639,l28; penicillin derivatives as illustrated by Ezekiel U.K. Patent l,389,089; propynylthio derivatives of benzimidazoles, pyrimidines, etc., as illustrated by von Konig et al U.S. Patent 3,910,791; combinations of iridium and rhodium compounds as disclosed by Yamasue et al U.S. Patent 3,901,713; sydnones or sydnone imines as illustrated by Noda et al U.S. Patent 3,88l,939; thiazolidine derivatives as illustrated by Ezekiel U.K. Patent l,458,197 and thioether-substituted imidazoles as illustrated by *Research Disclosure*, Vol. l36, August, 1975, Item 13651.

Apart from the features that have been specifically discussed the tabular grain emulsion preparation procedures, the tabular grains that they produce, and their further use in photography can take any convenient conventional form. Substitution 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 tabular grain emulsions, being also feasible in many types of photographic applications. The low levels of native blue sensitivity of the high chloride {100} tabular grain emulsions of the invention 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.

Photographic elements containing high chloride {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.

Examples

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

Example 1

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

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

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

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

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 0.5 mole percent iodide, based on silver. Fifty percent of total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.84 mm 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.

Example 2 (Comparative)

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

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

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

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

Examples 3 and 4

These examples demonstrate the effectiveness of iridium as a dopant to reduce low intensity reciprocity failure (LIRF) when the iridium is located very near the grain surface. In these examples LIRF was measured by comparing 1/10 and 10 second exposures. Three individual silver iodochloride {100} tabular grain emulsions were prepared for use in these examples. Table I describes the grain dimensions and iodide content.

Table I

Emulsion	Iodide %	Average Thickness (μm)	Average ECD (μm)
S-1	0.04	0.15	1.48
S-2	0.07	0.13	1.43
S-3	0.07	0.12	1.45

The dopants used in combination with the emulsions S-1, 2 and 3 to improve LIRF are given in Table II.

Table II

Dopant	Chemical Formula
D-1	K_3IrCl_6
D-2	$K_4Ir_2Cl_{10}$
D-3	$K_6Ir_6Cl_{24}$

The examples that follow describe the use of these dopants in various amounts and in various locations during the sensitization of emulsions S-1 to S-3.

The sensitized emulsions were coated onto cellulose acetate film support. The coating format was an emulsion layer comprised of 200 mg/ft^2 (21.5 mg/dm^2) of the tabular silver chloride emulsion dispersed in 500 mg/ft^2 (53.8 mg/dm^2) of gelatin; an overcoat comprised of 100 mg/ft^2 (10.8 mg/dm^2) gelatin and a hardener, bis(vinylsulfonylmethyl)ether at a level of 0.5% by weight, based on total gelatin.

The coated photographic elements were evaluated for reciprocity response by giving them a series of calibrated (total energy) exposures ranging from 1/10 of a second to 10 seconds. The exposed film was processed for 6 minutes in a hydroquinone-Elon™ (*p*-N-methylaminophenol hemisulfate) developer.

Example 3

This example demonstrates the usefulness of dopant D-2 added during spectral sensitization by means of a pCl cycle which is comprised of sequential addition of chloride ion, D-2, and silver ion. The introduction of the dopant in the pCl cycle produces an emulsion with improved LIRF behavior as compared to either an emulsion that is spectrally sensitized without use of the dopant or the pCl cycle or an emulsion that is spectrally sensitized with the pCl cycle, but with the dopant omitted, where the emulsions are otherwise the same.

Emulsion S-1 was spectrally sensitized by treating a portion with 550 mg per mole of silver of blue spectral sensitizing dye Dye SS-1 followed by heat digestion. APMT was added thereafter at an amount of 90 mg per silver mole. This represents the control emulsion.

Other portions of S-1 were spectrally sensitized in a similar manner, except that a pCl cycle of 2 mole % chloride ion and D-2 addition followed by 2 mole % silver ion addition was performed to effect the incorporation of D-2. Such a pCl cycle was accomplished either before or after the treatment of S-1 with the sensitizing dye. These samples constitute examples of the invention.

A final example was prepared in which a pCl cycle without dopant was performed to demonstrate the effect of the 2 mole % cycle, free of any dopant effects.

Table III summarizes the photographic results of various amounts of D-2 added via a pCl cycle technique.

Table III

Ex. 3 Part #	cycle before/after dye	D-2 micro- gram. per mole	Speed		LIRF
			365 nm	whitelight	
3/1	none	none	160	160	30
3/2	after	none	171	158	23
3/3	after	15	164	151	23
3/4	after	50	150	134	8
3/5	after	100	150	134	5
3/6	before	15	169	160	18
3/7	before	50	161	152	15
3/8	before	100	161	152	13

From Table III it is apparent that the use of D-2 reduces LIRF of the emulsion. Speed is reported in Tables III, IV, VI and XVIII as 100 times the log of the exposure required to give a density of 0.15 above the minimum density.

Example 4

This example demonstrates the usefulness of dopants D-1, D-2 and D-3 in reducing LIRF when added via a pCl cycle technique to the spectral and chemical sensitization of emulsions S-2 and S-3.

Separate portions of S-2 and S-3 were spectrally and chemically sensitized by treating each portion with 550 mg per mole of silver of blue spectral sensitizing dye Dye SS-1 followed by a heat digestion. Then 2 mg per mole of a colloidal gold sulfide reagent were added followed by heat digestion for 30 minutes at 60 °C. Thereafter, the temperature was adjusted to 40 °C, and 90 mg per mole of APMT were added. The resulting parts represent the undoped emulsions for comparison to the doped emulsions.

Another undoped example was prepared in a similar manner, except a 2 mole % pCl cycle consisting of chloride ion followed by silver ion was performed after the dye addition and digestion steps, but before the chemical sensitization step.

Other portions were spectrally and chemically sensitized, given a pCl cycle with various amounts of dopant added, then treated with APMT as described above.

The photographic results showing the LIRF improvements of the parts containing the dopants D-1, D-2 and D-3 is documented in Table IV. Also noteworthy is the significant speed increases that are obtained with certain amounts of D-1 and D-3.

Table IV

Ex. 4 Part #	Emulsion	vAg cycle	Dopant	Amount ug/mole Ag	White light speed	LIRF
4/1	S-2	none	none	0	221	25
4/2	S-2	Yes	none	0	231	19
4/3	S-2	Yes	D-2	1500	205	6
4/4	S-2	Yes	D-2	5000	155	4
4/5	S-3	none	none	0	221	20
4/6	S-3	Yes	D-1	15	231	12
4/7	S-3	Yes	D-1	50	230	8
4/8	S-3	Yes	D-1	100	233	14
4/9	S-3	Yes	D-1	200	218	12
4/10	S-3	Yes	D-3	5	243	9
4/11	S-3	Yes	D-3	15	265	4
4/12	S-3	Yes	D-3	50	239	2
4/13	S-3	Yes	D-3	100	230	1

Example 5

This example demonstrates the effectiveness of iridium to reduce LIRF when incorporated during precipitation with a silver bromide Lippmann emulsion.

The host high chloride {100} tabular grain emulsion employed Emulsion S-3, described in Example 4.

Lippmann silver bromide emulsions (of approximately 0.08 μm edge length) were prepared with and without incorporated dopants. Table V lists the Lippmann emulsions used and the dopant type and amount contained in each emulsion. By blending doped and undoped Lippmann emulsions a variety of dopant concentrations were available for incorporation onto the host AgCl {100} T-grain emulsion.

Table V

Lippmann Emulsion	Size (μm)	Dopant Formula	Dopant abbreviation	Amount MPPM
L-1	0.08	undoped	---	0
L-2	0.09	K_3IrCl_6	D-1	200
L-3	0.09	$K_4Ir_2Cl_{10}$	D-2	100

Portions of host emulsion S-3 were spectrally and chemically sensitized by treating each portion with 550 mg per mole of silver of blue spectral sensitizing dye Dye SS-1 followed by a heat digestion. Two mg per silver mole of a colloidal gold sulfide reagent were added followed by heat digestion for 30 minutes at 60 °C. Thereafter, the temperature was adjusted to 40 °C and 90 mg per silver mole of APMT were added. The resulting parts represent the undoped emulsions provided for comparison.

Another comparative emulsion was prepared in a similar manner to that described above, except that 2 mole % of an undoped Lippmann silver bromide emulsion were added after the colloidal gold sulfide and heat digestion. Once the Lippmann emulsion was added an additional heat digestion of 10 minutes at 60 °C was performed. Then the temperature was lowered to 40 °C, and 90 mg per silver mole of APMT was added. This comparative example was provided to demonstrate the effect of an undoped Lippman bromide on the S-3 host emulsion.

Other portions of the S-3 host emulsion were sensitized as the above comparative example, except that doped Lippmann silver bromide emulsions or blends of doped and undoped Lippmann silver bromide emulsions were added and digested for 10 minutes at 60 °C. Table VI shows the LIRF benefit when the doped Lippmann additions were made.

Coating, exposure and process were undertaken as described in Example 4.

Table VI

Ex. 5 Part #	2% Lippmann bromide	Dopant Type	Amount of dopant (PPM)	White light speed	LIRF
5/1	none	none	0	221	20
5/2	Yes	none	0	233	20
5/3	Yes	D-1	0.8	230	16
5/4	Yes	D-1	2.0	238	10
5/5	Yes	D-1	4.0	244	12
5/6	Yes	D-2	0.4	237	17
5/7	Yes	D-2	1.0	231	15
5/8	Yes	D-2	2.0	239	11

As demonstrated in Table VI, the treatment of the high chloride {100} tabular grain host emulsion with iridium doped Lippmann silver bromide emulsions results in a significant reduction in LIRF.

Example 6

This example demonstrates an emulsion according to the invention in which 90% 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% 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 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 10 minutes with the temperature remaining at 40 °C. Following the hold, a 0.5 M silver nitrate solution and a 0.5 M NaCl solution were then added simultaneously at 8 mL/min for 40 minutes with the pCl being maintained at 2.35. 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 2.35.

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

This example demonstrates an emulsion prepared similarly as the emulsion of Example 3, but an initial 0.08 mole percent iodide and a final 0.04% iodide.

A 2030 mL solution containing 3.52% 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 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 10 minutes with the temperature remaining at 40 °C. Following the hold, a 0.5 M silver nitrate solution and a 0.5 M sodium chloride solution were then added simultaneously at 8 mL/min for 40 minutes with the pCl being maintained at 2.95.

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

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

A 2030 mL solution containing 3.52% 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 10 minutes with 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 then added simultaneously at 2 mL/min for 40 minutes with the pCl being maintained at 2.35.

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

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% 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 2.2.

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 10 minutes with 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 then added simultaneously at 8 mL/min while a 3.375×10^{-2} M potassium iodide was simultaneously added at 14.6 mL/min for 10 minutes with the pCl being maintained at 2.35.

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

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% 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 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 10 minutes with 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 then added simultaneously at 8 mL/min for 40 minutes with the pCl being maintained at 2.60 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 mm, a mean thickness of 0.034 μm, a mean aspect ratio of 11.3 and a mean tabularity of 363.

Example 11

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

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 10 minutes with 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

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

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 sodium 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 with 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 % iodide. About 65% of the total projected grain area was provided by tabular grains having an average diameter of 1.5 μm and an average thickness of 0.18 μm.

Example 13

This example compares the photographic performance of a {100} silver chloride tabular emulsion according to the invention to a silver chloride cubic grain emulsion of similar average grain volume.

Emulsion A. Silver iodochloride tabular emulsion with {100} major faces

Precipitation (a remake of the Example 3 emulsion scaled up 3X)

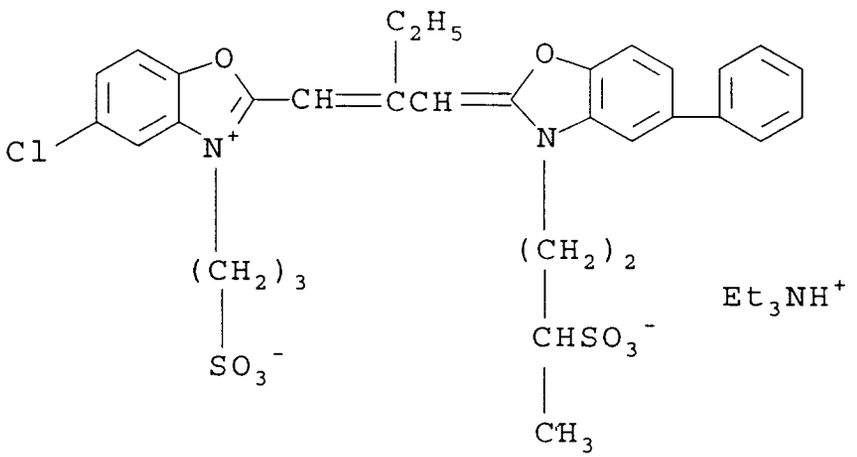
A 6090 ml solution containing 3.52% by weight of low methionine gelatin, 0.0056 M sodium chloride and 1.48 x 10^{-4} potassium iodide was provided in a stirred reaction vessel at 40 °C. While the solution was vigorously stirred, 90 mL of 2.0 M silver nitrate and 90 mL of a 1.99 M sodium chloride and 0.01 M potassium iodide solution were added simultaneously at a rate of 180 mL/min each. The mixture was then

held for 10 minutes with the temperature remaining at 40 °C. Following the hold, a 0.5 M silver nitrate solution and a 0.5 M sodium chloride solution were added simultaneously at 24 mL/min for 40 minutes followed by a linear acceleration from 24 mL/min to 48 mL/min over 130 minutes, while maintaining the pCl at 2.35. The pCl was then adjusted to 1.30 with sodium chloride then washed using ultrafiltration to a pCl of 2.0 then adjusted to a pCl of 1.65 with sodium chloride. The resulting emulsion was a tabular grain silver chloride emulsion contained 0.06 mole percent iodide and had a mean equivalent circular grain diameter of 1.45 μm and a mean grain thickness of 0.13 μm.

Sensitization

An optimum green light sensitization was found for Emulsion A by conducting numerous small scale finishing experiments where the level of sensitizing dye, sodium thiosulfate pentahydrate, aurous dithiosulfate dihydrate and the hold time at 65 °C were varied. The optimum finish was as follows: to a 0.5 mole portion of Emulsion A melted at 40 °C and well stirred, 0.800 mmol/mole of green light sensitizing dye A was added followed by a 20 minute hold. To this was added 0.10 mg/mole of sodium thiosulfate pentahydrate and 0.20 mg/mole of sodium aurous dithiosulfate dihydrate. The temperature was then increased to 65 °C over 9 minutes and then held for 4 minutes at 65 °C and rapidly cooled to 40 °C.

Sensitizing Dye A



Emulsion B. Silver chloride cubic grain emulsion (Control)

Precipitation

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

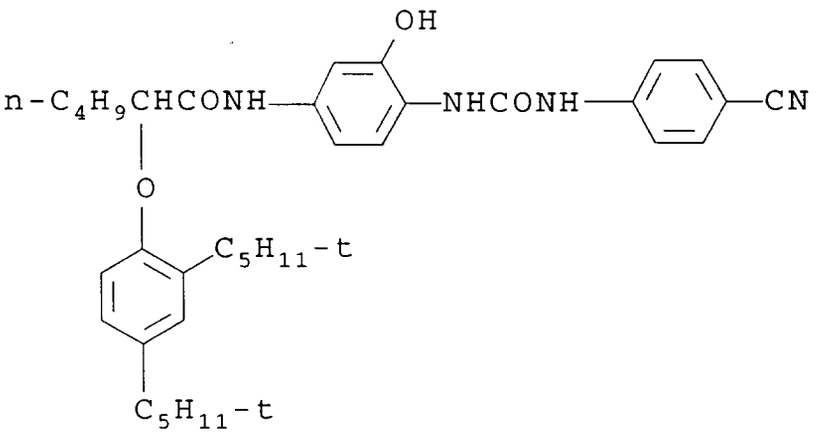
Sensitization

An optimum green light sensitization was found in the same manner as described for Emulsion A. The conditions for the optimum were as follows: to a 0.05 mole quantity of Emulsion B melted at 40 °C and well stirred, 0.2 mmol/mole of sensitizing dye A was added followed by a 20 minute hold. To this was added 0.25 mg/mole of sodium thiosulfate pentahydrate and 0.50 mg/mole of sodium aurous dithiosulfate dihydrate. The temperature was then increased to 65 °C over 9 minutes and held for 10 minutes followed by rapid cooling to 40 °C.

Photographic Performance

Each of the sensitized emulsions was coated on antihalation support at 0.85 g/m^2 of silver along with 1.1 g/m^2 of cyan dye-forming coupler C and 2.7 g/m^2 of gelatin. This was overcoated with 1.6 g/m^2 of gelatin and hardened with 1.7 weight percent, based on total gelatin, of bis(vinylsulfonylmethyl)ether. The coatings were evaluated for intrinsic sensitivity by exposing for 0.02 seconds in a step wedge sensitometer with the 365 nm line of a mercury vapor lamp as the light source. Sensitivity to green light was measured by exposing the coatings for 0.02 seconds using a step wedge sensitometer with a 3000 °K tungsten lamp filtered to simulate a Daylight V light source and filtered to transmit only green and red light by a Kodak Wratten ™ 9 filter (transmitting wavelengths longer than 450 nm). The coatings were processed using the Kodak Flexicolor ™ C-41 color negative process, described in *Brit. J. Photog. Annual* 1988, p196-198 , and the dye density was measured using status M red filtration.

Coupler C



The photographic results are summarized in Table VII.

Table VII

Emulsion	365 line exposure			Wratten ™ 9 exposure		
	Dmin	Rsens	contrast	Dmin	Rsens	contrast
Emulsion A (tab.)						
unsensitized	0.06	10	1.75	---	---	---
green sensitized	0.22	129	1.96	.22	371	2.08
Emulsion B (cubic)						
unsensitized	0.06	7	4.03	---	---	---
green sensitized	0.22	120	2.89	.16	128	2.86

Table VII shows that for intrinsic sensitivity as measured by the 365 line exposure, both Emulsions A and B are very similar as would be expected based on their similar grain volume. Comparing the green light sensitivity as measured by the Wratten ™ 9 exposures shows that the tabular emulsion is 2.9 times more sensitive to green light than the cubic emulsion. This clearly shows the advantage of the tabular morphology.

Example 14

This example describes the sensitization and photographic performance of a {100} silver chloride tabular emulsion and a silver chloride cubic emulsion of similar average grain volume sensitized using gold sulfide and a blue spectral sensitizing dye, and compared in low silver coatings on a resin coated paper

support.

Precipitation of Silver chloride tabular emulsion with {100} major faces

This emulsion was prepared in an identical fashion to the {100} silver chloride tabular emulsion described in Example 13.

Precipitation of Silver chloride cubic emulsion

This emulsion was prepared in a similar fashion to the cubic emulsion described in Example 13, except the ripener 1,8-dithiadioctanediol was omitted and flow rates and precipitation time were adjusted to achieve the same size emulsion.

Sensitization

Both emulsions were sensitized to blue light using the following procedures. A quantity of each emulsion was melted at 40 °C, 660 mg/mole Ag of sensitizing dye B was added to the {100} tabular emulsion and 220 mg/mole of the same dye was added to the cubic emulsion based on their specific surface area, followed by a 20 minute hold. 2.0 mg/mole of aurous sulfide was added to each emulsion followed by a 5 minute hold. The temperature was then raised to 60 °C and held for 30 minutes after which 90 mg/mole of APMT was added and the emulsion was chill set.

Photographic Performance

Each of the sensitized emulsions was coated on resin coated paper support at 0.28 g/m^2 of silver along with 1.1 g/m^2 of yellow dye forming coupler B and 0.82 g/m^2 of gelatin. The coatings were evaluated for intrinsic sensitivity by exposing for 0.1 seconds in a step wedge sensitometer with the 365 nm line of a mercury vapor lamp as the light source. Sensitivity to white light was measured by exposing the coatings for 0.1 seconds using a step wedge sensitometer with a 3000 °K tungsten lamp. The coatings were processed using a standard RA-4 color paper process as described in *Research Disclosure,* Vol. 308, p.933, 1989. Dye density was measured using standard reflection geometry and status A filtration.

The photographic results are summarized in Table VIII.

Table VIII

Emulsion	365 line exposure			3000°K Tungsten exposure		
	Dmin	Rsens	contrast	Dmin	Rsens	contrast
{100} tabular	0.08	98	2.53	.08	154	2.53
cubic	0.11	100	2.64	.11	100	2.64

Table VIII shows that for intrinsic sensitivity as measured by the 365 line exposure, both the cubic and the tabular emulsion are similar in sensitivity, as would be expected based on their similar grain volume. Comparing the white light sensitivity as measured by the 3000 °K tungsten exposures shows that the tabular emulsion is about 50% more sensitive to blue light than the cubic emulsion.

Example 15

This example shows how bromide can be added at the end of the precipitation or during the finish to produce emulsions with surface halide structure and/or growths. These emulsions show good photographic performance.

Emulsion A (Invention)

This emulsion was prepared identically to the {100} tabular emulsion described in Example 13. A quantity of this emulsion was then melted at 40 °C and 1200 mg/mole of potassium bromide was rapidly added. 0.6 mmol of green sensitizing dye A per mole of emulsion was then added followed by a 20 minute

hold. 1.0 mg/mole of sodium thiosulfate pentahydrate and 1.3 mg/mole of potassium tetrachloroaurate were then added followed by a temperature ramp to 60 °C and a 10 minute hold. The emulsion was then cooled to 40 °C and 70 mg/mole of APMT was added and the emulsion was chill set. Examination of the crystals by scanning electron microscopy revealed that the edges of the crystal had been roughened by the bromide deposition and some surface roughening was also present.

Emulsion B (Invention)

This emulsion illustrates the precipitation and sensitization of a {100} silver chloride tabular emulsion where potassium bromide was added during the final step of the precipitation to form an emulsion whereby the majority of the grains have epitaxial deposits located at 3 or 4 of the 4 available tabular grain corners.

Precipitation

A 1536 mL solution containing 3.52% by weight low methionine gelatin, 0.0056 M sodium chloride and 2.34×10^{-4} M potassium iodide was provided in a stirred reaction vessel at 40 °C and pH 5.74. While this solution was vigorously stirred, 30 mL of 2.0 M silver nitrate and 30 mL of 2.0 M sodium chloride were added simultaneously at a rate of 60 mL/min each. This achieved grain nucleation.

The mixture was then held for 10 seconds after which a 0.5 M silver nitrate and a 0.5 M sodium chloride solution were added simultaneously at 5.3 mL/min for 60 minutes with the pCl maintained at 2.35. The silver nitrate and sodium chloride solutions were then added using linearly accelerated flow rates from 5.3 mL/min to 15.6 mL/min over 150 minutes.

The pCl was then adjusted to 1.55 with sodium chloride and 25g of phthalated deionized gel was added and dissolved. The pH was then reduced to 3.85 and the stirring was stopped to allow the coagulum to settle. The supernatant was discarded and distilled water was added back to the coagulum to bring it to its original volume at the end of the precipitation. Stirring was resumed and the pH was adjusted back to 5.36 and the pCl was 2.45.

With vigorous stirring, 39 mL of 1.5 M potassium bromide solution was added over 30 minutes bringing the pCl to 1.8.

The pH was adjusted to 5.8 and 25g of phthalated deionized gel was added and dissolved. The pH was reduced to 3.85 and stirring was stopped to allow the coagulum to settle. The supernatant was removed, 27g of low methionine gel was added and the emulsion weight was raised to 800g with distilled water. The pH was adjusted to 5.77 and the pCl to 1.65 with 1.0 M sodium chloride solution.

The resulting emulsion had a mean equivalent circular diameter of 1.67mm and a mean grain thickness of 0.135mm. The halide composition was 93.964% silver chloride, 6.0% silver bromide and 0.0036% silver iodide. Seventy-five percent of the grains had three or more minor edges with epitaxial deposits.

Sensitization

A 0.15 mole quantity of emulsion was melted at 40 °C with stirring. To this was added 0.70 mmol/mole of green sensitizing dye A followed by a 20 minute hold. To this was added 1.0 mg/mole of sodium thiosulfate pentahydrate and 1.3 mg/mole of potassium tetrachloroaurate. The temperature was then increased to 60 °C over 12 minutes and held for 5 minutes followed by rapid cooling to 40 °C. 70 mg/mole of APMT was then added and the emulsion was chill set.

Emulsion C

This example illustrates the precipitation and sensitization of a {100} silver chloride tabular emulsion where potassium bromide was added during the final step of the precipitation to form an emulsion where the majority of the grains had epitaxial deposits located at only 1 or 2 of the minor edges.

Precipitation

A 1536 mL solution containing 3.52% by weight low methionine gelatin, 0.0056 M sodium chloride and 2.34×10^{-4} M potassium iodide was provided in a stirred reaction vessel at 40 °C and pH 5.74. While this solution was vigorously stirred, 30 mL of 2.0 M silver nitrate and 30 mL of 2.0 M sodium chloride were added simultaneously at a rate of 60 mL/min each. This achieved grain nucleation.

The mixture was then held for 10 seconds after which a 0.5 M silver nitrate and a 0.5 M sodium chloride solution were added simultaneously at 8.0 mL/min for 40 minutes with the pCl maintained at 2.35. The silver nitrate and sodium chloride solutions were then added using linearly accelerated flow rates from 8.0 mL/min to 16.1 mL/min over 130 minutes.

The pCl was then adjusted to 1.65 by running the sodium chloride solution at 20 mL/min for 8.0 min. This was followed by a 10 minute hold. The pCl was then increased back to 2.15 by running the silver nitrate solution at 5.0 mL/min for 27.7 min. This was followed by the addition of a 1.5 M potassium bromide solution at 2.0 mL/min over 20 minutes bringing the pCl to 1.70.

25 g of phthalated deionized gel was then added and dissolved. The pH was reduced to 3.85 and stirring was stopped to allow the coagulum to settle. The supernatant was removed and distilled water was added back to original volume. The pH was then adjusted back to 5.7 with vigorous stirring resumed. The pH was then adjusted back to 3.8 and the stirring was again stopped to allow the coagulum to form. The supernatant was again discarded and 20g of low methionine gel was added and the emulsion weight was raised to 800g with distilled water. The pH was adjusted to 5.77 and the pCl to 1.65 with 1.0 M sodium chloride solution.

The resulting emulsion had a mean equivalent circular diameter of 1.65mm and a mean grain thickness of 0.14mm. The halide composition was 93.964% silver chloride, 6.0% silver bromide and 0.0036% silver iodide. Examination of the emulsion by scanning electron microscopy showed that 97 percent of the grains had epitaxial depositions visible on two or fewer of the four available host tabular grain corners.

Sensitization

The sensitization was identical to that used in Example B, except the level of sodium thiosulfate pentahydrate and potassium tetrachloroaurate were increased by 50%.

Emulsion D (Control)

This emulsion was composed of silver chloride cubic grains and was precipitated identically to the cubic emulsion in Example 13 and is of similar grain volume to the three tabular emulsions in this example. This emulsion was sensitized as follows: a quantity was melted at 40 °C and 500 mg/mole of potassium bromide was added followed by 0.2 mg/mole of sensitizing dye A and a 20 minute hold. To this was added 0.25 mg/mole of sodium thiosulfate pentahydrate and 0.50 mg/mole of sodium aurous dithiosulfate dihydrate followed by a temperature ramp to 65 °C and a 12 minute hold. The emulsion was then quickly chilled.

Photographic Performance

Each of the sensitized emulsions was coated on antihalation support at 0.85 g/m^2 of silver along with 1.1 g/m^2 of cyan dye forming coupler C and 2.7 g/m^2 of gelatin. This was overcoated with 1.6 g/m^2 of gelatin and hardened with bis(vinyl-sulfonylmethyl)ether at 1.75% of the total coated gelatin weight. The coatings were evaluated for intrinsic sensitivity by exposing for 0.02 seconds in a step wedge sensitometer with the 365 nm line of a mercury vapor lamp as the source. Sensitivity to green light was measured by exposing the coatings for 0.02 seconds using a step wedge sensitometer with a 3000 °K tungsten lamp filtered to simulate a Daylight V source and filtered to transmit only light with wavelengths longer than 400 nm by a Kodak Wratten ™ 2B filter. The coatings were then processed using a Kodak Flexicolor ™ C-41 color negative process. The dye density was measured using status M red filtration.

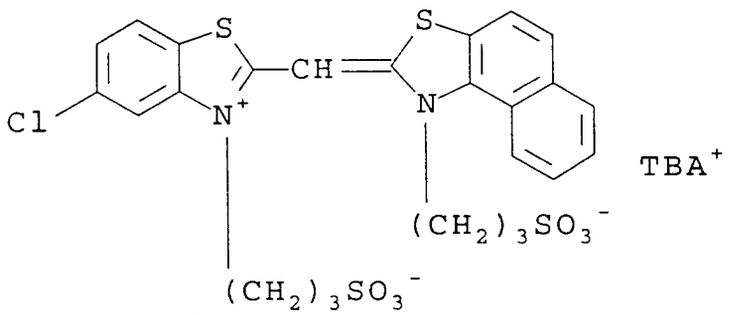
The photographic results are tabulated and summarized in Table IX.

Table IX

Emulsion	Wratten™ 2B exposure			365 line exposure		
	Dmin	Rsens	contrast	Dmin	Rsens	contrast
Emulsion A	.14	200	2.22	.12	60	1.87
Emulsion B	.13	275	2.05	.14	141	1.89
Emulsion C	.12	245	2.36	.13	79	2.65
Emulsion D (control)	.14	100	2.82	.18	100	2.48

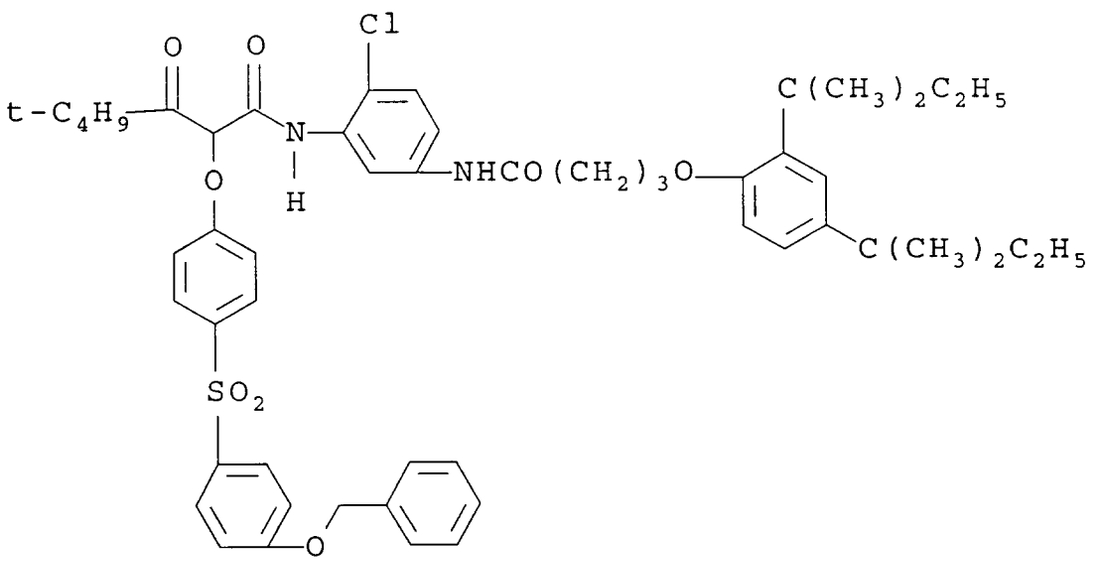
Table IX shows all of the {100} tabular grain emulsion examples are at least 2 times more sensitive to a white light exposure than the similarly sensitized cubic grain emulsion even though emulsion A and C showed less intrinsic sensitivity to the 365 mercury line exposure.

Sensitizing Dye B



TBA^+ = tributylammonium

Coupler Y



Example 16 (Comparison)

The purpose of this Example is to demonstrate the inability of a ripening out procedure--specifically the procedure referred to in the 1963 Torino Symposium, cited above--to produce a tabular grain emulsion satisfying the requirements of the invention.

To a reaction vessel containing 75 mL distilled water, 6.75 g deionized bone gelatin and 2.25 mL of 1.0 M NaCl solution at 40 °C were simultaneously added with efficient stirring 15 mL of 1.0 M $AgNO_3$ solution and 15 mL of 1.0 M NaCl solution each at 15 mL per minute. The mixture was stirred at 40 °C for 4 minutes, then the temperature was increased to 77 °C over a period of 10 minutes and 7.2 mL of 1.0 M NaCl solution were added. The mixture was stirred at 77 °C for 180 minutes and then cooled to 40 °C.

The resulting grain mixture was examined by optical and electron microscopy. The emulsion contained a population of small cubes of approximately 0.2 μm edge length, large nontabular grains, and tabular grains with square or rectangular major faces. In terms of numbers of grains the small grains were overwhelmingly predominant. The tabular grains accounted for no more than 25 percent of the total grain projected area of the emulsion.

The mean thickness of the tabular grain population was determined from edge-on views obtained using an electron microscope. A total of 26 tabular grains were measured and found to have a mean thickness of 0.38 μm. Of the 26 tabular grains measured for thickness, only one had a thickness of less than 0.3 μm, the thickness of that one tabular grain being 0.25 μm.

Example 17

This example has as its purpose to demonstrate successful preparation of an emulsion satisfying the requirements of the invention employing commercially available deionized gelatin as a starting material.

To a reaction vessel, equipped with a stirrer, were added 2865 g of distilled water containing 20 g of deionized gelatin (purchased from Rousellot™). The initial calcium ion level was 8×10^{-6} molar. Additional calcium ion was added to the reaction vessel as calcium chloride hydrate to compensate for calcium ion removal during deionization of the gelatin, thereby bringing the calcium ion concentration up to 2.36 millimolar. Adjustment of the dispersing medium within the reaction vessel was completed by adding 0.96 g of sodium chloride and 45 g of 0.012 molar potassium iodide solution. The pH was adjusted to 6.5 at 55 °C and maintained at that value throughout the precipitation by addition of sodium hydroxide or nitric acid solutions.

A 4.0 M silver nitrate and a 4.0 M sodium chloride solution were added for 30 seconds at a rate consuming 5 percent of the total silver. The emulsion was then held at 62 °C for 10 minutes followed by the addition of 5000 g of a solution containing 1.6 percent of the deionized gelatin. This was followed by simultaneous addition of the silver nitrate and sodium chloride with the flow rates linearly increased by a factor of 2.58 over 70 minutes with the pAg maintained at 6.37. The total amount of silver iodochloride precipitated was 4.745 moles.

Greater than 80 percent of total grain projected area was accounted for by tabular grains. The tabular grains exhibited an average ECD of 1.65 μm, an average thickness of 0.165 μm, and an average aspect ratio of 10.

When the preparation procedure described above was repeated with calcium acetate substituted for calcium chloride hydrate, greater than 85 percent of total grain projected area was accounted for by tabular grains. The tabular grains exhibited an average ECD of 1.5 μm, an average thickness of 0.16 μm, and an average aspect ratio of 9.4. When magnesium, aluminum or iron ions were substituted for calcium ions in the dispersing medium, emulsions satisfying the requirements of the invention were also obtained.

Examples 18 and 19

These examples demonstrate the preparation of high (> 25) tabularity, intermediate aspect ratio tabular grain emulsions by the process of the invention.

Example 18

A 6090 mL solution containing 3.52% by weight of low methionine gelatin, 0.0056 M sodium chloride and 1.48×10^{-4} potassium iodide was provided in a stirred reaction vessel at 40 °C. While the solution was vigorously stirred, 90 mL of 2.0 M silver nitrate and 90 mL of a 1.99 M sodium chloride and 0.01 M potassium iodide solution were added simultaneously at a rate of 180 mL/min each. The mixture was then held for 10 minutes with the temperature remaining at 40 °C. Following the hold, a 1.0 M silver nitrate solution and a 1.0 M sodium chloride solution were added simultaneously at 12 mL/min for 40 minutes followed by a linear acceleration from 12 mL/min to 33.7 mL/min over 233.2 minutes, while maintaining the pCl at 2.25. The pCl was then adjusted to 1.30 with sodium chloride then washed using ultrafiltration to a pCl of 2.0 then adjusted to a pCl of 1.65 with sodium chloride. The resulting emulsion was a tabular grain

silver chloroiodide emulsion contained 0.03 mole percent iodide with a mean equivalent circular grain diameter of 1.51 μm and a mean thickness of 0.22 μm. The resulting average aspect ratio was 6.9 and the average tabularity was 31.

Example 19

A 1536 mL solution containing 3.52% by weight of low methionine (hydrogen peroxide treated) gelatin, 0.0056 M sodium chloride, 2.34 x 10^{-4} M potassium iodide, and 0.3 mL of a polyethylene glycol antifoamant was provided in a stirred reaction vessel at 40 °C. While the solution was vigorously stirred, 30 mL of 2.0 M silver nitrate and 30 mL of a 2.0 M sodium chloride solution were added simultaneously at a rate of 60 mL/min each. The mixture was then held for 10 seconds. 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 maintained at 2.25. The pCl was then adjusted to 1.65 with 1.0 M sodium chloride. The 0.5 M silver nitrate and the 0.5 M sodium chloride were then each added at a linearly increasing the flow rate, commencing at 8 mL/min and increasing at a rate of 0.0615 mL/min while maintaining pCl at 1.65. After 90 minutes microscopic observation of the emulsion showed an equivalent circular diameter of 0.9 μm with a mean grain thickness of 0.17 mum. The average aspect ratio at this point was 5.3 and the tabularity was 31.

Examples 20 and 21

These examples demonstrate the preparation of emulsions satisfying the requirements of the invention employing a dual-zone growth process in which the growth reactants are premixed in a continuous reactor prior to being added to the growth reactor, to yield tabular grains with an ECD greater than 2 μm.

Example 20

To a stirred reaction vessel containing a 2945 mL solution that is 1.77 percent by weight bone gelatin, 0.0056 M sodium chloride, 1.86 x 10^{-4} M potassium iodide and at 55 °C and pH 6.5, 15 mL of a 4.0 M silver nitrate solution and 15 mL of a 4.0 M sodium chloride solution were each added concurrently at a rate of 30 mL/min.

The mixture was then held for 5 minutes during which 7000 mL of distilled water were added and the temperature was raised to 65 °C, while the pCl was adjusted to 2.15 and the pH to 6.5. Following the hold, the size of the resulting grains was increased through growth using a dual-zone process. In this process, a solution of 0.67 M silver nitrate was premixed with a 0.67 M solution of sodium chloride and a solution of 0.5 percent by weight bone gelatin at a pH of 6.5, in a continuous reactor with a total volume of 30 mL, which was well-mixed. The effluent from this premixing reactor was then added to the original reaction vessel, which during this step acted as a growth reactor. During the growth step the fine crystals from the continuous reactor were ripened onto the original crystals through Ostwald ripening. The total suspension volume of the growth reactor during this growth step was maintained constant at 13.5 L using ultrafiltration.

The flow rates of the 0.67 M silver nitrate solution and the 0.67 M sodium chloride solution were linearly increased from 20 to 80 mL/min, 150 mL/min and 240 mL/min in 25 minute intervals. The flow rate of the 0.5 percent gelatin reactant was maintained constant at 500 mL/min. The continuous reactor in which these reactants were premixed was kept at 30 °C and a pCl of 2.45, while the growth reactor was maintained at a temperature of 65 °C, a pCl of 2.15, and a pH of 6.5.

This procedure resulted in 6 moles of a high aspect ratio tabular grain iodochloride emulsion containing 0.01 mole % iodide. More than 90% of the total projected grain area was provided by tabular grains having {100} major faces, an average ECD of 2.55 μm, and an average thickness of 0.165 μm. Therefore, the tabular grain population had an average aspect ratio of 15.5 and an average tabularity of 93.7.

Example 21

Silver iodochloride nuclei were formed in a 30 mL well-mixed, continuous reactor by mixing a 0.447 M silver nitrate solution (at 100 mL/min) with a 0.487 M sodium chloride and 0.00377 M potassium iodide solution (at 100 mL/min) and a 2.0 percent by weight bone gelatin solution (at 1 L/min) at a pCl of 2.3 and a temperature of 40 °C. The resulting mixture containing the nuclei was transferred to a stirred semi-batch reactor for 1.5 min. The semi-batch reactor was maintained at 65 °C and a constant volume of 13.5 L (using ultrafiltration) and was initially at a pCl of 2.15, a pH of 6.5 and a bone gelatin concentration of 0.37 percent by weight. During the nuclei transfer from the continuous reactor to the semi-batch reactor the pCl of the

latter was maintained at 2.15 by the addition of a 1 M sodium chloride solution.

After holding for 5 min, growth of the initial nuclei was achieved by the dual-zone process as follows. A solution of 0.67 M silver nitrate, a solution of 0.67 M sodium chloride and a solution of 0.5 percent by weight bone gelatin at a pH of 6.5 were premixed in the 30 mL continuous reactor, and then transferred to the semi-batch reactor. Growth occurred by Ostwald ripening whereby the crystals from the continuous reactor were dissolved in the semi-batch reactor and the original nuclei increased in size. The total suspension volume of the semi-batch reactor was maintained constant at 13.5 L during this step, as during the nucleation step.

During the growth step the flow rates of the 0.67 M silver nitrate solution and the 0.67 M sodium chloride solution were linearly increased from 20 to 80 mL/min, 150 mL/min and 240 mL/min in 25 minute intervals. The flow rate of the 0.5 percent gelatin reactant was maintained constant at 500 mL/min. The continuous reactor in which these reactants were premixed was kept at 30 °C and a pCl of 2.45, while the growth reactor was maintained at a temperature of 65 °C, a pCl of 2.15, and a pH of 6.5.

This procedure resulted in 6 moles of a large, high aspect ratio tabular grain iodochloride emulsion containing 0.01 mole % iodide. More than 80% of the total projected grain area was provided by tabular grains having {100} major faces, an average ECD of 2.28 μm, and an average thickness of 0.195 μm. Therefore, the tabular grain population had an average aspect ratio of 11.7 and an average tabularity of 60.0.

Claims

1. A radiation sensitive emulsion containing a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population projected area, characterized in that at least 50 percent of total grain projected area is accounted for by tabular grains (1) bounded by {100} major faces having adjacent edge ratios of less than 10, (2) each having an aspect ratio of at least 2, and (3) containing on average at least one pair of metal ions chosen from group VIII, periods 5 and 6, at adjacent cation sites in their crystal lattice.

2. A radiation sensitive emulsion according to claim 1 further characterized in that at least five pairs of adjacent cation sites of said crystal lattice are occupied by said group VIII metal ions.

3. A radiation sensitive emulsion according to claim 2 further characterized in that at least ten pairs of adjacent cation sites of said crystal lattice are occupied by said group VIII metal ions.

4. A radiation sensitive emulsion according to any one of claims 1 to 3 inclusive further characterized in that said group VIII metal ions are iridium ions.

5. A radiation sensitive emulsion according to any one of claims 1 to 4 inclusive further characterized in that said grains contain at least one group of from 2 to 20 of said group VIII metal ions each occupying a cation site position within the face centered cubic crystal lattice structure adjacent at least one other of said group VIII metal ions.

6. A radiation sensitive emulsion according to any one of claims 1 to 5 inclusive further characterized in that said grains contain at least one group of from 6 to 10 of said group VIII metal ions each occupying a cation site position within the face centered cubic crystal lattice structure adjacent at least one other said group VIII metal ions.

7. A radiation sensitive emulsion according to any one of claims 1 to 6 inclusive further characterized in that said face centered cubic lattice structure contains anions between said adjacent cation site group VIII metal ions differing from remaining anions in said face centered cubic crystal lattice structure.

8. A radiation sensitive emulsion according to claim 7 further characterized in that said anions between said adjacent cation site group VIII metal ions are halide ions.

9. A process of preparing a radiation sensitive emulsion containing a dispersing medium and silver halide grains, characterized in that at least 50 percent of total grain projected area is accounted for by tabular grains (1) bounded by {100} major faces having adjacent edge ratios of less than 10, (2) each having an aspect ratio of at least 2, (3) containing on average at least one pair of metal ions chosen from

group VIII, periods 5 and 6, at adjacent cation sites in their crystal lattice, and (4) internally at their nucleation site containing iodide and at least 50 mole percent chloride are prepared by the steps comprised of

(a) introducing silver and halide salts into a dispersing medium so that nucleation of the tabular grains occurs in the presence of iodide with chloride accounting for at least 50 mole percent of the halide present in the dispersing medium and the pCl of the dispersing medium being maintained in the range of from 0.5 to 3.5,

(b) following nucleation completing grain growth under conditions that maintain the {100} major faces of the tabular grains, and

(c) during at least one of steps (a) and (b) introducing into the dispersing medium oligmers of group VIII, period 5 or 6, metal, wherein each oligomer contains at least two metal ions and on average at least two metal ions are incorporated in each grain in adjacent cation sites.

10. A process according to claim 9 further characterized in that the anionic oligomers are selected from among those satisfying the formulae:

M_2L_{10}
M_6L_{24}
$M8L_{32}$

and

$M_{10}L_{38}$

where

M represents a group VIII, period 5 or 6, element

and

L represents a bridging ligand.



FIG. 1



FIG. 2

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 10 4411

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y D	EP-A-0 436 249 (EASTMAN KODAK COMPANY) & US-A-5 024 931 (EVANS ET AL.) * page 3, line 2 - line 18; claims 1-20; example 4 *	1-10	G03C1/005
Y P	DATABASE WPI Week 9151, Derwent Publications Ltd., London, GB; AN 91374154 & JP-A-3 252 649 (FUJI PHOTO FILM K.K.) 11 November 1991 * abstract * & US-H-1294 (YAMADA et al.)	1-10	
D,Y	US-A-4 063 951 (T.G.BOTT) * column 2, line 63 - line 68 *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13 July 1994	Buscha, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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