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(54) High tabularity high chloride emulsions of exceptional stability.

(57) A radiation sensitive emulsion is disclosed containing a silver halide grain population comprised of at least 50 mole percent chloride, based on total silver forming the grain population. Greater than 30 percent of the grain population projected area is accounted for by tabular grains having a thickness of less than 0.3 µm and having {100} major faces. In one preferred form of the invention tabular grains are formed by nucleation 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.

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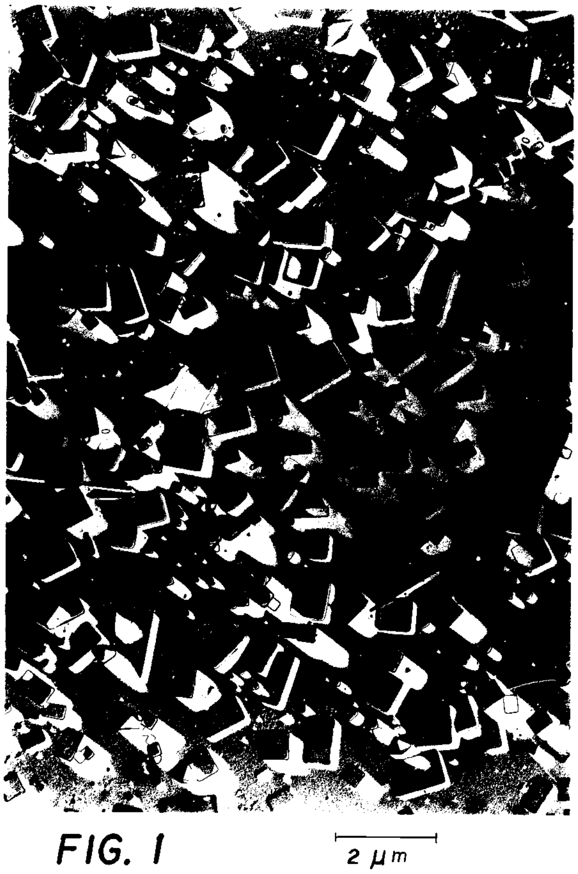


FIG. 1

The invention relates to silver halide photography. More specifically, the invention relates to radiation sensitive silver halide emulsions useful in photography.

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

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 realized by increasing the proportions of selected tabular grain populations in photographic emulsions.

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

An emulsion is generally understood to be a "high aspect ratio tabular grain emulsion" when tabular grains having a thickness of less than 0.3 μm have an average aspect ratio of greater than 8 and account for greater than 50 percent of total grain projected area. The difficulty in achieving high average aspect ratios in high chloride tabular grain emulsions has often led to accepting average aspect ratios of greater than 5 as the best available approximations of high average aspect ratios. 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. High chloride thin tabular grain emulsions have been difficult to prepare and ultrathin high chloride tabular grain emulsions have been completely unknown.

In almost every instance tabular grain emulsions satisfying grain thickness (**t**), average aspect ratio (**ECD/t**), average tabularity (**ECD/t^2**) and projected area aims have been formed by introducing two or more parallel twin planes into octahedral grains during their preparation. Regular octahedral grains are bounded by {111} crystal faces. The predominant feature of tabular grains formed by twinning are opposed parallel {111} major crystal faces. The major crystal faces have a three fold symmetry, typically appearing triangular or hexagonal.

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

Wey U.S. Patent 4,399,215 produced the first silver chloride high aspect ratio (ECD/t > 8) tabular grain emulsion. The tabular grains were of the twinned type, exhibiting major faces of three fold 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.

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 three fold symmetry of conventional tabular grain {111} major crystal faces. Bogg employed an ammoniacal ripening process for preparing the tabular grains, thereby encountering the grain thickening and pH disadvantages discussed above in connection with Wey. Bogg conceded the process was feasible for producing individual grain aspect ratios no higher than 7:1. Thus, the average aspect ratio of a tabular grain emulsion so produced would necessarily be substantially less than 7. This is corroborated by Example 3 (the only emulsion described with grain features numerically characterized). The average aspect ratio of the emulsion was 2, with the highest aspect ratio grain (grain A in Figure 3) being only 4. Bogg stated that the emulsions can contain no more than 1 percent iodide and demonstrated only a 99.5% bromide 0.5% iodide emulsion.

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). Mignot relies on excess bromide ion for ripening. Since silver bromide exhibits a solubility approximately two orders of magnitude lower than that of silver chloride, reliance on excess bromide ion for ripening precludes the formation of high chloride tabular grains.

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.

In one aspect this 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, in which greater than 30 percent of the grain population projected area is accounted for by tabular grains having a mean thickness of less than 0.3 μm. The emulsion is characterized in that the tabular grains have parallel major faces lying in {100} crystallographic planes.

In a preferred form, of the tabular grains bounded by {100} major faces a portion accounting for 50 percent of total grain projected area selected on the criteria of adjacent major face edge ratios of less than

10 and thicknesses of less than 0.3 µm and having higher aspect ratios than any remaining tabular grains satisfying these criteria have an average aspect ratio of greater than 8.

In another aspect this invention is directed to a process of preparing silver halide emulsions of the second preferred form containing tabular grains bounded by {100} major faces comprised of the steps of (1) introducing silver and halide salts into a dispersing medium and (2) maintaining conditions within the dispersing medium that promote the formation of tabular grains bounded by {100} major faces. The process is characterized in that of the tabular grains bounded by {100} major faces a portion accounting for 50 percent of total grain projected area selected on the criteria of adjacent major face edge ratios of less than 10 and thicknesses of less than 0.3 µm and having higher aspect ratios than any remaining tabular grains satisfying these criteria (1) have an average aspect ratio of greater than 8 and (2) internally at their nucleation site contain iodide and at least 50 mole percent chloride, at least the selected portion of the tabular grains being formed by nucleation 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.

The invention in one preferred form is based on 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 high aspect ratio tabular grain emulsion in which the tabular grains are bounded by {100} crystal faces.

Not only does the preferred form of the invention represent the discovery of a novel process for preparing tabular grain emulsions, the emulsions that are produced by the process are novel. Further, alternative processes of preparation are disclosed that do not require the presence of iodide during grain nucleation and hence render iodide incorporation within the high chloride tabular grains of the invention a matter of choice. The invention places within the reach of the art tabular grains bounded by {100} crystal faces with halide contents, halide distributions and grain thicknesses that have not been heretofore realized. The present invention provides the first ultrathin tabular grain emulsion in which the grains are bounded by {100} crystal faces. The invention provides 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 high chloride emulsions, the present invention extends beyond high chloride emulsions to those containing a wide range of bromide, iodide and chloride concentrations.

Brief Description of the Drawings

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

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

Figure 3 is a carbon replica electron photomicrograph of grains of Example 11A.

Figure 4 is a scanning electron photomicrograph of grains of Example 11B viewed perpendicular to the support.

Figure 5 is a scanning electron photomicrograph of grains of Example 11B viewed at 60° angle to the support.

The invention is directed to a photographically useful, 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, in which greater than 30 percent of the grain population projected area is accounted for by tabular grains tabular grains having a mean thickness of less than 0.3 µm. The tabular grains have parallel major faces lying in {100} crystallographic planes.

In a preferred form of the invention, of the tabular grains bounded by {100} major faces those accounting for 50 percent of the total grain projected area, selected on the criteria of (1) adjacent major face edge ratios of less than 10, (2) thicknesses of less than 0.3 µm and (3) higher aspect ratios than any remaining tabular grains satisfying criteria (1) and (2), have an average aspect ratio of greater than 8.

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. Some of these grains are regular cubic grains. That is, they are grains that have three mutually perpendicular edges of equal length. To distinguish cubic grains from tabular grains it is necessary to measure the grain shadow lengths. From a knowledge of the angle of illumination (the shadow angle) it is possible to calculate the thickness of a grain from a measurement of its shadow length. The projected areas of the cubic grains are included in determining total grain projected area.

To quantify the characteristics of the tabular grains, a grain-by-grain examination of each of the remaining grains presenting square or rectangular faces is required. The projected area of each grain is noted for determination of total grain projected area.

Each of the grains having a square or rectangular face and a thickness of less than 0.3 μm is examined. The projected area (the product of edge lengths) of the upper surface of each grain is noted. From the grain projected area the ECD of the grain is calculated. The thickness (t) of the grain and its aspect ratio (ECD/t) of the grain are next calculated.

After all of the grains having a square or rectangular face and a thickness of less than 0.3 mm have been measured, these grains are rank ordered according to aspect ratio. The grain with the highest aspect ratio is rank ordered first and the grain with the lowest aspect ratio is rank ordered last.

Proceeding from the top of the aspect ratio rank ordering, sufficient tabular grains are selected to account for 50 percent of total grain projected area. The aspect ratios of the selected tabular grain population are then averaged. In the emulsion of Figure 1 and in the emulsions of the invention the average aspect ratio of the selected tabular grain population is greater than 8. In preferred emulsions according to the invention average aspect ratios of the selected tabular grain population are greater than 12 and optimally at least 20. Typically the average aspect ratio of the selected tabular grain population ranges up to 50, but higher aspect ratios of 100, 200 or more can be realized.

The selected tabular grain population accounting for 50 percent of total grain projected area 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 is selected on the basis of tabular grain thicknesses of less than 0.2 μm instead of 0.3 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 of up 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 selected 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 equivalent circular diameter (**ECD**) to thickness (**t**). This relationship has been expressed quantitatively in terms of aspect ratio (**ECD/t**). 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 tabulity;
AR is aspect ratio;
ECD is effective circular diameter in micrometers (μm); and
t is grain thickness in micrometers.

The selected tabular grain population accounting for 50 percent of total grain projected area exhibits a tabularity of greater than 25 and preferably greater than 100. Since the selected 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 selected tabular grain population can exhibit an average ECD of any photographically useful magnitude compatible with a tabularity of greater than 25. 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. A minimum ECD to satisfy minimum tabularity requirements with a minimum grain thickness of the selected tabular grain population is just greater than 0.25 μm. 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 selected population of tabular grains satisfying the parameters noted above accounts for at least 30 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 thicknesses of less than 0.3 μm and {100} major faces is increased. The preferred emulsions according to the invention are those in which at least 50 percent, most preferably 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 that satisfy the selected tabular grain descriptions above are specifically contemplated.

If tabular grains having a thickness of less than 0.3 μm do not account for at least 30 percent (preferably at least 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. Emulsions containing thicker (up to 0.5 μm) tabular grains with {111} major faces, though generally inferior, have been suggested for use in the art to maximize capture of light in the spectral region to which silver halide exhibits native sensitivity (e.g., blue light). Emulsions containing thicker tabular grains having {100} major faces can be applied, if desired, to similar applications.

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

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

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

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

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

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

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

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

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

It is possible, but not preferred, to introduce silver chloride or silver chloroiodide 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, preferably in a pH range of from 5,0 to 7.0. 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, the disclosure of which is here incorporated by reference. *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). 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 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 thiocyanate 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.

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.

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*.

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 bromochloride, silver iodochloride, silver iodobromochloride and silver bromoiodochloride emulsions, where halides are named in order of increasing concentrations. 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.

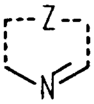
Although not essential to the practice of the invention, a further procedure that can be employed to maximize the population of tabular grains having {100} major faces is to incorporate an agent capable of restraining the emergence of non-{100} grain crystal faces in the emulsion during its preparation.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

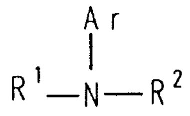


where

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

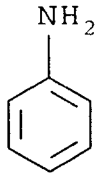
Ar is an aromatic ring structure containing from 5 to 14 carbon atoms and

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.

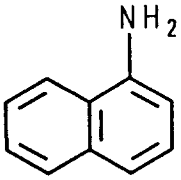
The following are representative of compounds contemplated satisfying formulae I and/or II:

R-1



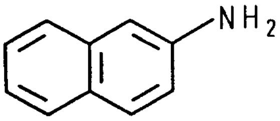
aniline

RA-2



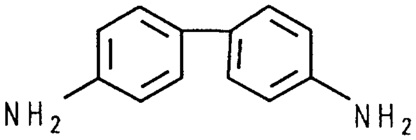
α-naphthylamine

RA-3



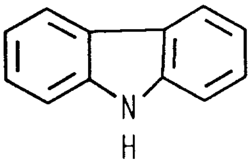
β-naphthylamine

RA-4



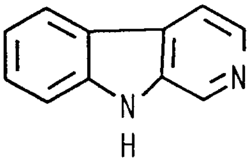
benzidine

RA-5



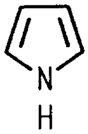
carbazole

RA-6



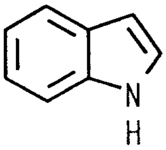
norharman

RA-7



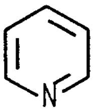
pyrrole

RA-8



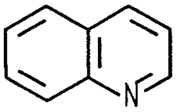
indole

RA-9



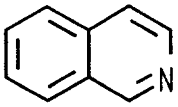
pyridine

RA-10



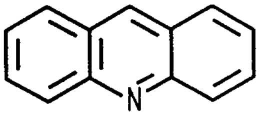
quinoline

RA-11



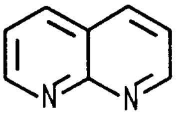
isoquinoline

RA-12



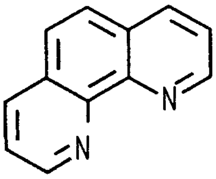
acridine

RA-13



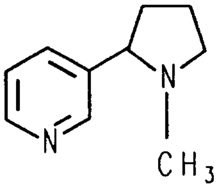
1,8-naphthyridine

RA-14



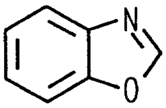
1,10-phenanthroline

RA-15



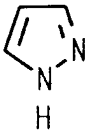
nicotine

RA-16



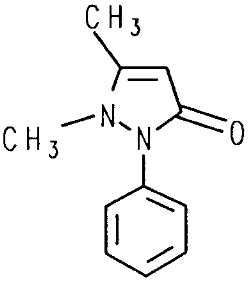
benzoxazole

RA-17



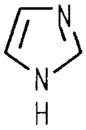
pyrazole

RA-18



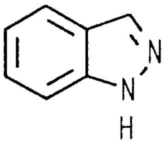
antipyrine

RA-19



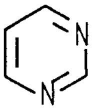
imidazole

RA-20



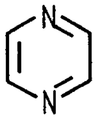
indazole

RA-21



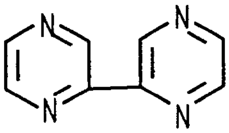
pyrimidine

RA-22



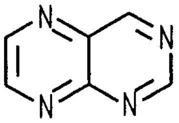
pyrazine

RA-23



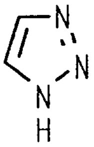
2,2'-bipyrazine

RA-24



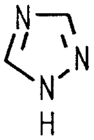
pteridine

RA-25



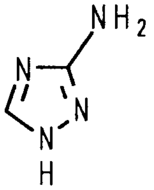
1,2,3-triazole

RA-26



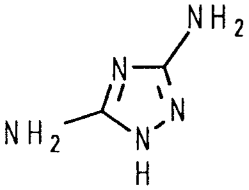
1,2,4-triazole

RA-27



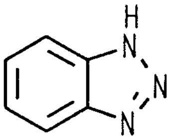
3-amino-1,2,4-triazole

RA-28



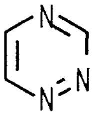
3,5-diamino-1,2,4-triazole

RA-29



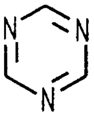
benzotriazole

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 ent 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).

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. Such conventional features are 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.

Examples

The invention can be better appreciated by reference to the following examples.

Example 1 (Invention)

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.

Example 3 (Invention)

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 2.25. The 0.5 M $AgNO_3$ solution and the 0.5 M NaCl solution were then added simultaneously with a ramped linearly increasing flow from 8 mL per minute to 16 mL per minute over 130 minutes with the pCl maintained at 2.25.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 0.06 mole percent iodide, based on silver. Fifty percent of total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 1.86 µm and an average thickness of 0.082 µm, selected on the basis of an aspect ratio rank ordering of all {100} tabular grains having a thickness of less than 0.3 µm and a major face edge length ratio of less than 10. The selected tabular grain population had an average aspect ratio (ECD/t) of 24 and an average tabularity (ECD/t^2) of 314. The ratio of major face edge lengths of the selected tabular grains was 1.2. Ninety three percent of total grain projected area was made up of tabular grains having {100} major faces and aspect ratios of at least 7.5. These tabular grains had a mean ECD of 1.47 µm, a mean thickness of 0.086 µm, a mean aspect ratio of 17.5 and a mean tabularity of 222.

Example 4 (Invention)

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 2.25.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 0.04 mole percent iodide, based on silver. Fifty percent of the total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.67 µm and an average thickness of 0.035 µm, selected on the basis of an aspect ratio rank ordering of all {100} tabular grains having a thickness of less than 0.3 µm and a major face edge length ratio of less than 10. The selected tabular grain population had an average aspect ratio (ECD/t) of 20 and an average tabularity (ECD/t^2) of 651. The ratio of major face edge lengths of the selected tabular grains was 1.9. Fifty two percent of total grain projected area was made up of tabular grains having {100} major faces and aspect ratios of at least 7.5. These tabular grains had a mean ECD of 0.63 µm, a mean thickness of 0.036 µm, a mean aspect ratio of 18.5 and a mean tabularity of 595.

Example 5 (Invention)

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 3.00×10^{-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 2.25.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 1.6 mole percent iodide, based on silver. Fifty percent of total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.57 µm and an average thickness of 0.036 µm, selected on the basis of an aspect ratio rank ordering of all {100} tabular grains having a thickness of less than 0.3 µm and a major face edge length ratio of less than 10. The selected tabular grain population had an average aspect ratio (ECD/t) of 16.2 and an average tabularity (ECD/t^2) of 494. The ratio of major face edge lengths of the selected tabular grains was 1.9. Sixty two percent of total grain projected area was made up of tabular grains having {100} major faces and aspect ratios of at least 7.5. These tabular grains had a mean ECD of 0.55 µm, a mean thickness of 0.041 µm, a mean aspect ratio of 14.5 and a mean tabularity of 421.

Example 6 (Invention)

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 2.3.

While this solution was vigorously stirred, 30 mL of 1.0 M silver nitrate solution and 30 mL of a 0.99 M sodium chloride and 0.01 M potassium iodide solution were added simultaneously at a rate of 90 mL/min each. This achieved grain nucleation to form crystals with an initial iodide concentration of 2 mole percent, based on total silver.

The mixture was then held 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 3.75×10^{-3} M potassium iodide was simultaneously added at 14.6 mL/min for 10 minutes with the pCl being maintained at 1.95.

The resulting emulsion was a tabular grain silver iodochloride emulsion containing 5 mole percent iodide, based on silver. Fifty percent of total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.58 µm and an average thickness of 0.030 µm, selected on the basis of an aspect ratio rank ordering of all {100} tabular grains having a thickness of less than 0.3 µm and a major face edge length ratio less than 10. The selected tabular grain population had an average aspect ratio (ECD/t) of 20.6 and an average tabularity (ECD/t^2) of 803. The ratio of major face edge lengths of the selected tabular grains was 2. Eighty seven percent of total grain projected area was made up of tabular grains having {100} major faces and aspect ratios of at least 7.5. These tabular grains had a mean

ECD of 0.54 µm, a mean thickness of 0.033 µm, a mean aspect ratio of 17.9 and a mean tabularity of 803.

Example 7 (Invention)

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 2.25 to form crystals with an initial iodide concentration of 2 mole percent, based on total silver.

The resulting emulsion was a tabular grain silver iodobromochloride emulsion containing 0.27 mole percent iodide and 36 mole percent bromide, based on silver, the remaining halide being chloride. Fifty percent of total grain projected area was provided by tabular grains having {100} major faces having an average ECD of 0.4 µm and an average thickness of 0.032 µm, selected on the basis of an aspect ratio rank ordering of all {100} tabular grains having a thickness of less than 0.3 µm and a major face edge length ratio of less than 10. The selected tabular grain population had an average aspect ratio (ECD/t) of 12.8 and an average tabularity (ECD/t^2) of 432. The ratio of major face edge lengths of the selected tabular grains was 1.9. Seventy one percent of total grain projected area was made up of tabular grains having {100} major faces and aspect ratios of at least 7.5. These tabular grains had a mean ECD of 0.38 mm, a mean thickness of 0.034 µm, a mean aspect ratio of 11.3 and a mean tabularity of 363.

Example 8 (Invention)

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 3.1×10^{-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 9 (Invention)

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, 1.86×10^{-4} M KI and at 55° C and pH 6.5, 60 mL of a 4.0 M silver nitrate solution and 60.0 mL of a 4.0 M silver chloride solution were each added concurrently at a rate of 120 mL/min.

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

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 chloride tabular emulsion with {100} major faces

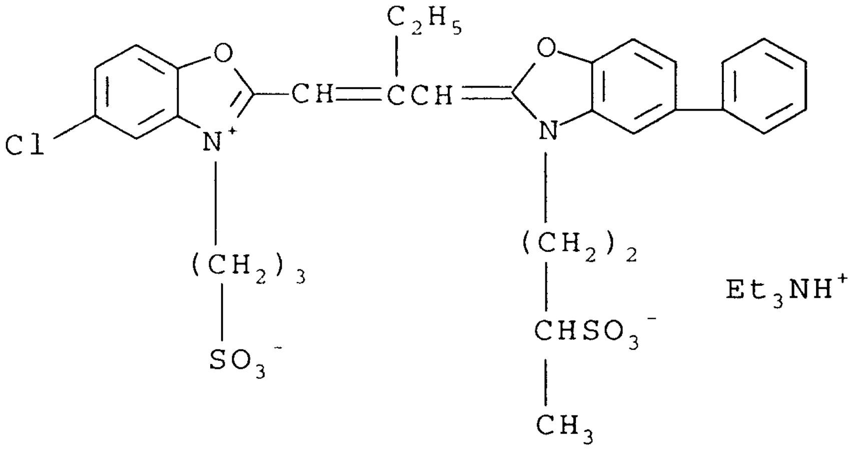
Precipitation (a remake of the Example 3 emulsion scaled up 3X)

A 6090 ml solution containing 3.52% by weight of low methionine gelatin, 0.0056 M sodium chloride and 1.48×10^{-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 2.25. 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 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.

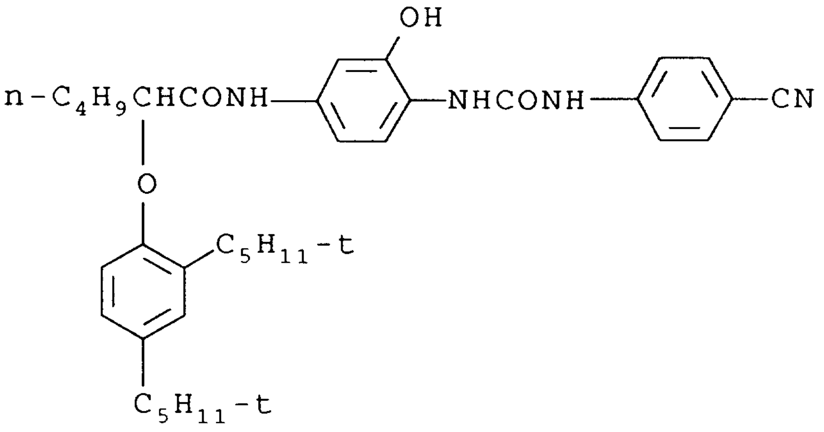
Sensitization

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(vinyl-sulfonylmethyl)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 a standard C-41™ color negative process and the dye density was measured using status M red filtration.

Coupler C



The photographic results are summarized in Table I.

Table I

Emulsion	365 line exposure Dmin	365 line exposure speed	365 line exposure contrast	Wratten 9™ exposure Dmin	Wratten 9™ exposure speed	Wratten 9™ exposure 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 I 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 11 High-Aspect-Ratio High-Chloride {100} Tabular Grain Emulsion

Example 11A

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

The resulting AgCl emulsion consisted of tabular grains having {100} major faces which made up 65% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.95 μm and a mean thickness of 0.165 μm. The average aspect ratio and tabularity were 11.8 and 71.7, respectively. This emulsion is shown in Fig. 3.

Example 11B

This emulsion was prepared similar to that of Example 11A except that the precipitation was stopped when 0.4 mole of Ag had been added.

The resulting emulsion consisted of tabular grain having {100} major faces which made up 65% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.28 µm and a mean thickness of 0.130 µm. The average aspect ratio and tabularity were 9.8 and 75.7, respectively. This emulsion is shown in Figs. 2 and 3.

Example 12 pH = 6.1 Nucleation, pH ≅ 3.6 Growth

This example was prepared similar to that of Example 11B except that the pH of the reaction vessel was adjusted to 3.6 for the last 95% of the $AgNO_3$ addition.

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

Example 13 High-Aspect-Ratio AgBrCl (10% Br) {100} Tabular-Grain Emulsion

This emulsion was prepared similar to that of Example 11B except that the salt solution was 3.6 M in NaCl and 0.4 M in NaBr.

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

Example 14 3,5-Diamino-1,2,4-Triazole as {100} Tabular Grain Nucleating Agent

This emulsion was prepared similar to that of Example 11A, except that 3,5-diamino-1,2,4-triazole (2.4 mmole) was used as the {100} tabular grin nucleating agent.

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

Example 15 Imidazole as {100} Tabular Grain Nucleating Agent

This emulsion was prepared similar to that of Example 11A except that imidazole (9.6 mmole) was used as the {100} tabular grain nucleating agent.

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

Example 16 AgCl{100} Tabular Grain Emulsion Made Without Aromatic Amine Restraining Agent

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

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

Example 17 Photographic Coatings

An emulsion was prepared similar to that of Example 11A except that the precipitation was scaled-up five times so that 4.0 moles of AgCl were precipitated. The resulting {100} tabular grain emulsion was cooled to 40 ° C, poured into 4 L of distilled water and allowed to gravity settle for 24 hours at 2 ° C. The settled phase was discarded. To the supernatant was added 12 g of phthalated gelatin and the emulsion was washed by the coagulation method of U.S. Patent 2,614,929.

The resulting 2.2 moles of emulsion consisted of tabular grains having {100} major faces which made up 80% of the projected area of the total grain population. This tabular grain population had a mean equivalent circular diameter of 1.81 μm and a mean thickness of 0.173 μm (measuring $>10^6$ grains). The average aspect ratio and tabularity were 10.5 and 60.5, respectively.

The emulsion was diluted to 1 Kg emulsion/mole AgCl and adjusted to a pAg of 7.42 with NaCl solution and pH of 5.3 at 40 ° C. It was divided into portions for spectral and chemical sensitizations.

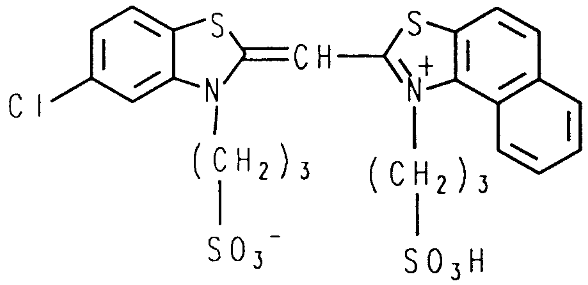
To portion designated A was added 0.5 mmole Dye A per mole AgCl.

To portion designated B was added 0.5 mmole Dye B per mole AgCl.

To portion designated C was added 0.5 mmole Dye A per mole AgCl.

To portion designated D was added 0.5 mmole Dye B per mole AgCl.

For the structure of Dye A refer to Example 10 above.



DYE B

To portions C and D was then added 10 mg Au_2S/mole AgCl. Next, 2.0 mole% NaBr, as a 1 M solution, was added to portions A, B, C and D. Portions C and D were heated for 20 minutes at 60 ° C. Scanning electron images show that all portions retained their {100} tabular grain content, and portion B had AgClBr epitaxial growths at the grains edges and corners. These portions were coated on polyester film support at 2.6 g silver/m^2 and 3.4 g gelatin/m^2 to make coatings A, B, C, and D, respectively. The coatings were exposed for 0.5 sec to a 600W 3,000 K tungsten light source through a 0-4.0 density step tablet and a Kodak Wratten™ filter. Coatings A and C were exposed through a Kodak Wratten™ 99 green filter while Coatings B an D were exposed through a Kodak Wratten™ 2B yellow filter. Another set of coatings were exposed on a variable wavelength, variable intensity wedge spectrograph.

The exposed coatings were processed in Kodak Developer DK-50™ for 5 min at 20 ° C. The results of the step tablet and wedge spectrographic exposure are given in Table II. These results show that high chloride {100} tabular grain emulsions can be made into photographic coatings. Additionally, this type of emulsion can be chemically and spectrally sensitized. Both blue and green spectral sensitization are demonstrated.

TABLE II

Coating	Dye	Chem. Sens.	D-max	Fog	Relative Speed at 0.2 Above Fog	Peak Spectral Response (nm)
A	A	No	1.77	0.09	100	550
C	A	Yes	1.51	0.15	128	550
B	B	No	1.64	0.08	100	480
C	B	Yes	1.41	0.49	204	480

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, in which greater than 30 percent of the grain population projected area is accounted for by tabular grains having a mean thickness of less than 0.3 µm,

   characterized in that the tabular grains have parallel major faces lying in {100} crystallographic planes.

2. A radiation sensitive emulsion according to claim 1 further characterized in that greater than 50 percent of the total grain projected area is accounted for by tabular grains having {100} major faces and a thickness of less than 0.3 µm.

3. A radiation sensitive emulsion according to claim 2 further characterized in that greater than 50 percent of the total grain projected area is accounted for by tabular grains having {100} major faces and a thickness of less than 0.2 µm.

4. A radiation sensitive emulsion according to claim 1 or 2 further characterized in that of the tabular grains bounded by {100} major faces a portion accounting for 50 percent of total grain projected area selected on the criteria of adjacent major face edge ratios of less than 10 and thicknesses of less than 0.3 µm and having higher aspect ratios than any remaining tabular grains satisfying these criteria (1) have an average aspect ratio of greater than 8 and (2) internally at their nucleation site contain iodide and at least 50 mole percent chloride.

5. A radiation sensitive emulsion according to claim 4 further characterized in that the selected portion of the tabular grains have an average aspect ratio of greater than 12.

6. A radiation sensitive emulsion according to claim 4 or 5 further characterized in that the selected portion of the tabular grains have adjacent major face edge ratios of less than 5.

7. A radiation sensitive emulsion according to claim 6 further characterized in that the selected portion of the tabular grains have adjacent major face edge ratios of less than 2.

8. A radiation sensitive emulsion according to any one of claims 4 to 7 inclusive further characterized in that the selected portion of the tabular grains are ultrathin tabular grains having thicknesses of less than 0.06 µm.

9. A radiation sensitive emulsion according to any one of claims 1 to 8 inclusive further characterized in that the tabular grains contain at least 90 mole percent chloride.

10. A process of preparing silver halide emulsions containing tabular grains bounded by {100} major faces of which the tabular grains bounded by {100} major faces a portion accounting for 50 percent of total grain projected area selected on the criteria of adjacent major face edge ratios of less than 10 and thicknesses of less than 0.3 µm and having higher aspect ratios than any remaining tabular grains satisfying these criteria (1) have an average aspect ratio of greater than 8 and (2) internally at their nucleation site contain iodide and at least 50 mole percent chloride, comprised of the steps of

    (1) 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 and

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

11. A process according to claim 10 further characterized in that bromide ion is present in the dispersing medium following grain nucleation.

12. A process according to claim 10 or 11 further characterized in that grain nucleation is undertaken in the presence of halide ions consisting essentially of chloride and iodide ions with the pCl of the dispersing

medium being in the range of from 1.0 to 3.0 and a gelatino peptizer being present having a methionine content of less than 30 micromoles per gram of peptizer.

13. A process according to claim 12 further characterized in that grain nucleation is undertaken in the presence of halide ions consisting essentially of chloride and iodide ions with the pCl of the dispersing medium being in the range of from 1.5 to 2.5 and a gelatino peptizer being present having a methionine content of less than 12 micromoles per gram of peptizer.

14. A process according to any one of claims 10 to 13 inclusive further characterized in that silver and halide salt solutions are introduced into the dispersing medium during grain nucleation and growth.

15. A process according to claim 14 further characterized in that the addition of the silver and halide salt solutions is suspended after grain nucleation to allow Ostwald ripening of grain nuclei and then resumed.

16. A process according to claim 14 or 15 further characterized in that chloride and iodide salt solutions are introduced into the dispersing medium during grain nucleation.

17. A process according to claim 15 or 16 further characterized in that bromide salt solution is introduced into the dispersing medium after salt solution introduction is resumed after the addition of the silver and halide salt solutions has been suspended to allow Ostwald ripening of grain nuclei.

FIG. 1

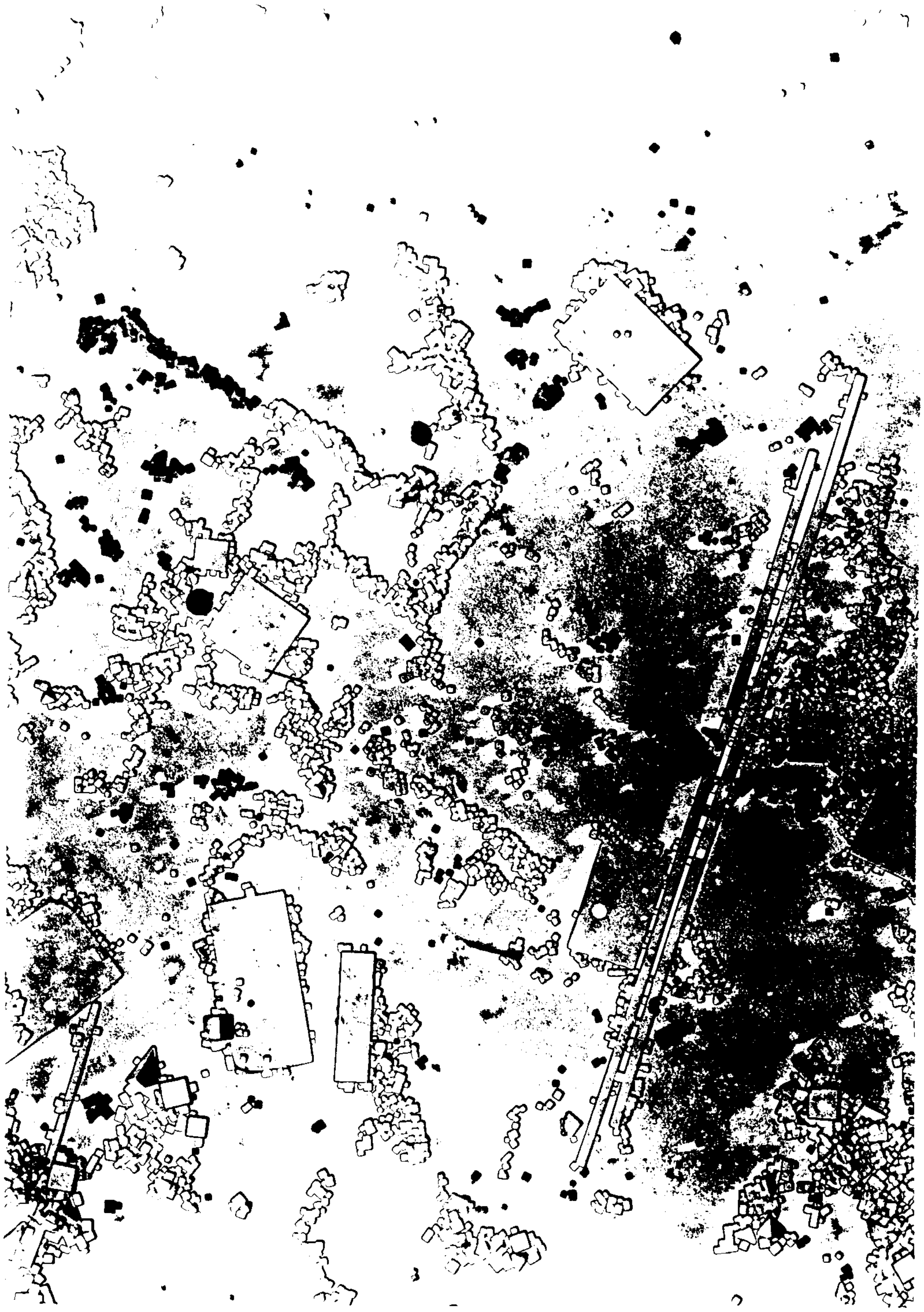
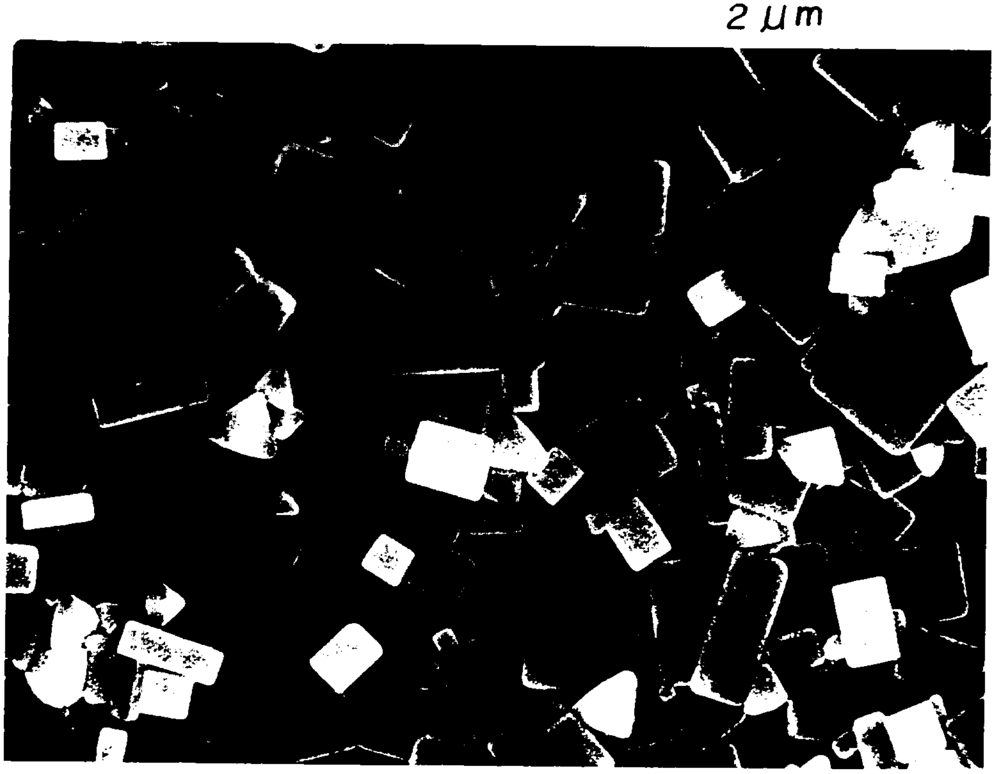


FIG. 2

FIG. 3



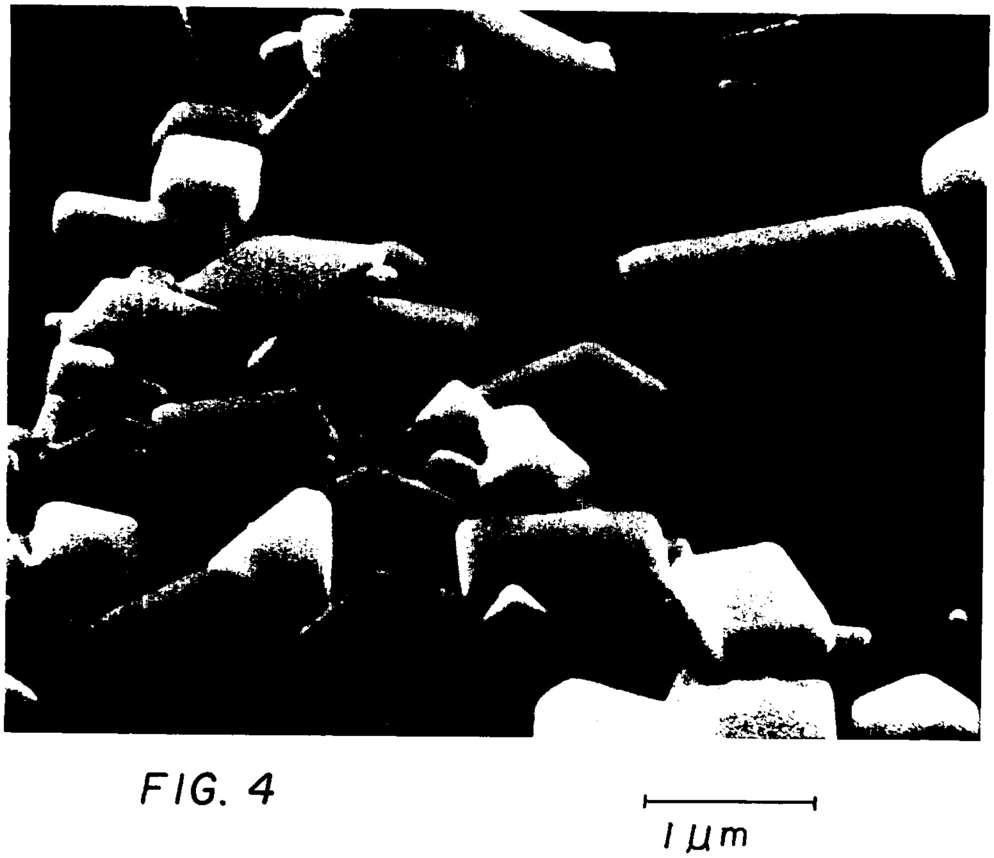


FIG. 4

FIG. 5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 11 6262

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)
D,X	US-A-4 063 951 (T.G.BOGG) * column 2, line 63 - line 68; claims 1-11 *	1-3,9	G03C1/005
X	PATENT ABSTRACTS OF JAPAN vol. 14, no. 169 (P-1032)(4112) 30 March 1990 & JP-A-20 24 643 (FUJI PHOTO FILM COMPANY LTD.) 26 January 1990 * abstract *	1-3	
D,A	US-A-4 386 156 (A.G.E.MIGNOT) * the whole document *	1-17	

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	28 DECEMBER 1993	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

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