

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

Publication number:

0 617 321 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **94104416.6**

(51)

Int. Cl.⁵: **G03C 1/005**(22) Date of filing: **21.03.94**(30) Priority: **22.03.93 US 35009**(43) Date of publication of application:
28.09.94 Bulletin 94/39(84) Designated Contracting States:
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(54) **Moderate aspect ratio tabular grain emulsions.**

(57) Silver halide emulsions are disclosed in which at least 50 percent of total grain projected area is accounted for by tabular grains (1) bounded by {100} major faces having adjacent edge ratios of less than 10, (2) each having an aspect ratio of at least 2 and together having an average aspect ratio of up to 8, and (3) internally at their nucleation site containing iodide and at least 50 mole percent chloride. The emulsions are prepared by a process comprised of the steps of (a) introducing silver and halide salts into a dispersing medium so that nucleation of the tabular grains occurs in the presence of iodide with chloride accounting for at least 50 mole percent of the halide present in the dispersing medium and the pCl of the dispersing medium being maintained in the range of from 0.5 to 3.5 and (b) following nucleation completing grain growth under conditions that maintain the {100} major faces of the tabular grains, grain growth being continued until the tabular grains have an average aspect ratio of up to 8.

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The invention relates to radiation sensitive silver halide emulsions.

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

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

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

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

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

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

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

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

significant bromide and iodide ion inclusions prepared starting with conventional and universally available peptizers.

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

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

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

In one aspect the invention is directed to a radiation sensitive emulsion comprised of a dispersing medium and silver halide grains, characterized in that at least 50 percent of total grain projected area is accounted for by tabular grains (1) bounded by {100} major faces having adjacent edge ratios of less than 10, (2) each having an aspect ratio of at least 2 and together having an average aspect ratio of up to 8, and (3) internally at their nucleation site containing iodide and at least 50 mole percent chloride.

The present invention 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 tabular grain emulsion in which the tabular grains are bounded by {100} crystal faces.

Not only does the invention represent the discovery of a novel process for preparing tabular grain emulsions, the emulsions that are produced by the process are novel. The invention places within the reach of the art tabular grains bounded by {100} crystal faces with halide contents, halide distributions and grain thicknesses that have not been heretofore realized. The invention is capable of providing tabular grain populations in any thickness optimum for a selected photographic application, ranging from ultrathin tabular grains to the thicknesses found in thicker tabular grains, sometimes referred to as slabular grains. The invention in one preferred form provides intermediate 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.

The photographically useful, radiation sensitive emulsions of the invention are comprised of a dispersing medium and silver halide grains. At least 50 percent of the total grain projected area is accounted for by tabular grains bounded by {100} major faces having adjacent edge ratios of less than 10. Tabular grains having {100} major faces are also hereinafter referred to as {100} tabular grains. By definition each {100} tabular grain exhibits an aspect ratio of at least 2. The {100} tabular grains have an average aspect ratio of up to 8, and internally at their nucleation site contain iodide and at least 50 mole percent chloride.

The identification of emulsions satisfying the {100} tabular grain projected area and aspect ratio requirements of the invention can be undertaken by analytical procedures that are well known in the art. For example, from a shadowed photomicrograph of carbon grain replicas of a representative emulsion of the invention, grains having {100} major faces can be readily identified from their orthogonal tetragonal (square or rectangular) major faces and/or projected areas. Nontabular grains either lack parallel grain faces or lack parallel major faces--that is, faces that are clearly larger than another face of the grain. Tabular grains with

{111} major faces exhibit a three fold symmetry. That is, the grains usually have triangular or hexagonal major faces and occasionally have polyhedral or nearly circular major faces, but in no instance do they exhibit orthogonal tetragonal major face.

Of the grains which have orthogonal tetragonal faces (i.e., {100} faces) a few grains may be observed that are acicular or rod-like grains (herein-after referred as rods). These grains are more than 10 times longer in one dimension than in any other dimension and are excluded from the tabular grain population based on their high ratio of edge lengths. The projected area accounted for by the rod-like grains is typically low.

After any rod-like grains present have been excluded based on the ratio of their adjacent edge lengths, the determination of which of the remaining grains with orthogonal tetragonal faces are {100} tabular grains requires determination of grain thickness. From a knowledge of the shadow angle it is possible to calculate the thickness of a grain from a measurement of its shadow length.

The {100} tabular grains are those grains having orthogonal tetragonal projected areas or major faces that exhibit an aspect ratio of at least 2. Aspect ratio (ECD/t) is the ratio of a grain's equivalent circular diameter (ECD) divided by its thickness (t). The ECD of a grain is the diameter of a circle having the same projected area as the grain. When tabular grains bounded by {100} major faces having adjacent edge ratios of less than 10 account for at least 50 percent of total grain projected area and exhibit an average aspect ratio of up to 8, the {100} tabular grain projected area and aspect ratio requirements of the invention are satisfied. Emulsions according to the invention that are highly useful for many photographic applications are those in which average aspect ratio is in the intermediate range--i.e., from 5 to 8.

The {100} tabular grain population preferably exhibits major face edge length ratios of less than 5 and optimally less than 2. The nearer the major face edge length ratios approach 1 (i.e., equal edge lengths) the lower is the probability of a significant rod population being present in the emulsion. Further, it is believed that tabular grains with lower edge ratios are less susceptible to pressure desensitization.

The tabular grain population can exhibit any grain thickness that is compatible with the average aspect ratios noted above.

Surprisingly, ultrathin tabular grain emulsions have been prepared satisfying the requirements of the invention. Ultrathin tabular grain emulsions are those in which the {100} tabular grain population is made up of tabular grains having thicknesses of less than 0.06 μm . It has been generally thought essential to form tabular grains by the mechanism of parallel twin plane incorporation to achieve ultrathin dimensions. Parallel twin planes produce tabular grains with {111} major faces. Emulsions according to the invention can be prepared in which the tabular grain population has a mean thickness down to 0.02 μm and even 0.01 μm . Ultrathin tabular grains have extremely high surface to volume ratios. This permits ultrathin grains to be photographically processed at accelerated rates. Further, when spectrally sensitized, ultrathin tabular grains exhibit very high ratios of speed in the spectral region of sensitization as compared to the spectral region of native sensitivity. For example, ultrathin tabular grain emulsions according to the invention can have entirely negligible levels of blue sensitivity, and are therefore capable of providing a green or red record in a photographic product that exhibits minimal blue contamination even when located to receive blue light.

For many photographic applications it is preferred that the {100} tabular grains accounting for at least 50 percent of total grain projected area have thicknesses of less than 0.3 μm and, optimally, less than 0.2 μm . It is appreciated that when the thicknesses of the tabular grains are limited the mean tabular grain ECD's of the emulsions are also limited. Thus, the mean ECD of {100} tabular grains having thicknesses of less than 0.3 μm or 0.2 μm is less than 2.4 μm or 1.6 μm , respectively.

There are specific photographic applications that can benefit by greater tabular grain thicknesses. For example, in constructing a blue recording emulsion layer of maximum achievable speed it is specifically contemplated that tabular grain thicknesses that are on average 1 μm or even larger, but preferably up to 0.8 μm , can be tolerated. This is because the eye is least sensitive to the blue record and hence higher levels of image granularity (noise) can be tolerated without objection. There is an additional incentive for employing larger grains in the blue record in that it is sometimes difficult to match in the blue record the highest speeds attainable in the green and red record. A source of this difficulty resides in the blue photon deficiency of sunlight. While sunlight on an energy basis exhibits equal parts of blue, green and red light, at shorter wavelengths the photons have higher energy. Hence on a photon distribution basis daylight is slightly blue deficient.

When tabular grain thicknesses are large (e.g., greater than 0.5 μm), the {100} tabular grain population can exhibit a mean ECD that ranges up to the highest photographically useful magnitudes. 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 . As is generally understood by those skilled in the art, tabular grain emulsions having higher ECD's are advantageous for achieving relatively high levels of photographic

sensitivity while tabular grain emulsions with lower ECD's are advantageous in achieving low levels of granularity.

5 So long as the population of tabular grains satisfying the parameters noted above accounts for at least 50 percent of total grain projected area a photographically desirable grain population is available. It is recognized that the advantageous properties of the emulsions of the invention are increased as the proportion of tabular grains having {100} major faces is increased. The preferred emulsions according to the invention are those in which at least 70 percent and optimally at least 90 percent of total grain projected area is accounted for by tabular grains having {100} major faces. When no significant grain population other than the {100} tabular grains are present in the emulsion, {100} tabular grain projected area can
10 approach 100 percent of the total grain projected area. If tabular grains do not account for 50 percent of the total grain projected area, the emulsion does not satisfy the requirements of the invention and is, in general, a photographically inferior emulsion.

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
15 for by any combination of coprecipitated grains. It is, of course, common practice in the art to blend emulsions to achieve specific photographic objectives. Blended emulsions in which at least one component emulsion satisfies the tabular grain descriptions above are specifically contemplated.

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
20 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.

25 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 crystal lattice irregularities in one or more of the cubic crystal faces. The cubic crystal faces that contain at least one crystal lattice irregularity thereafter accept silver halide at an accelerated rate as compared to the regular cubic crystal faces (i.e., those lacking the irregularity). When only one of the cubic crystal faces contains a crystal lattice irregularity, grain growth
30 on only one face is accelerated, and the resulting grain structure on continued growth is a rod. The same result occurs when only two opposite parallel faces of the cubic crystal structure contain the crystal lattice irregularity. However, when any two contiguous cubic crystal faces contain the crystal lattice irregularity, continued growth accelerates growth on both faces and produces a {100} tabular grain structure. It is believed that the tabular grains of the emulsions of this invention are produced by those grain nuclei having
35 two, three or four faces containing growth accelerating crystal lattice irregularities. Initially it was believed that the growth accelerating crystal lattice irregularities were screw dislocations, but more recent investigations have cast doubt on this explanation.

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
40 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.

45 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
50 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
55 to maintain the iodide ion concentration in the dispersing medium at the outset of nucleation at less than 10 mole percent. In fact, only minute amounts of iodide at nucleation are required to achieve the desired tabular grain population. Initial iodide ion concentrations of down to 0.001 mole percent are contemplated. However, for convenience in replication of results, it is preferred to maintain initial iodide concentrations of

at least 0.01 mole percent and, optimally, at least 0.05 mole percent.

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

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

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

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

The dispersing medium contained in the reaction vessel prior to the nucleation step is comprised of water, the dissolved halide ions discussed above and a peptizer. The dispersing medium can exhibit a pH within any convenient conventional range for silver halide precipitation, typically from 2 to 8. It is preferred, but not required, to maintain the pH of the dispersing medium on the acid side of neutrality (i.e., < 7.0). To minimize fog a preferred pH range for precipitation is from 2.0 to 6.0. Mineral acids, such as nitric acid or hydrochloric acid, and bases, such as alkali hydroxides, can be used to adjust the pH of the dispersing medium. It is also possible to incorporate pH buffers.

The peptizer can take any convenient conventional form known to be useful in the precipitation of photographic silver halide emulsions and particularly tabular grain silver halide emulsions. A summary of conventional peptizers is provided in *Research Disclosure*, Vol. 308, December 1989, Item 308119, Section IX. *Research Disclosure* is published by Kenneth Mason Publications, Ltd., Emsworth, Hampshire PO10 7DD, England. While synthetic polymeric peptizers of the type disclosed by Maskasky I, cited above and here incorporated by reference, can be employed, it is preferred to employ gelatino peptizers (e.g., gelatin and gelatin derivatives). As manufactured and employed in photography gelatino peptizers typically contain significant concentrations of calcium ion, although the use of deionized gelatino peptizers is a known practice. In the latter instance it is preferred to compensate for calcium ion removal by adding divalent or trivalent metal ions, such as alkaline earth or earth metal ions, preferably magnesium, calcium, barium or aluminum ions. Specifically preferred peptizers are low methionine gelatino peptizers (i.e., those containing less than 30 micromoles of methionine per gram of peptizer), optimally less than 12 micromoles of methionine per gram of peptizer, these peptizers and their preparation are described by Maskasky II and King et al, cited 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.

5 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
10 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
15 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
20 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
25 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
30 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
35 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
40 concentration in the dispersing medium. That is, it is preferred to lower the pCl of the dispersing medium into a range in which increased silver chloride solubility is observed. Alternatively, ripening can be accelerated and the percentage of total grain projected area accounted for by {100} tabular grains can be increased by employing conventional ripening agents. Preferred ripening agents are sulfur containing ripening agents, such as thioethers and thiocyanates. Typical thiocyanate ripening agents are disclosed by
45 Nietz et al U.S. Patent 2,222,264, Lowe et al U.S. Patent 2,448,534 and Illingsworth U.S. Patent 3,320,069, the disclosures of which are here incorporated by reference. Typical thioether ripening agents are disclosed by McBride U.S. Patent 3,271,157, Jones U.S. Patent 3,574,628 and Rosencrantz et al U.S. Patent 3,737,313, the disclosures of which are here incorporated by reference. More recently crown thioethers have been suggested for use as ripening agents. Ripening agents containing a primary or secondary amino
50 moiety, such as imidazole, glycine or a substituted derivative, are also effective. Sodium sulfite has also been demonstrated to be effective in increasing the percentage of total grain projected accounted by the {100} tabular grains.

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

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

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

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

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

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

The emulsions of the invention include silver iodochloride emulsions, silver iodobromochloride emulsions and silver iodochlorobromide emulsions. Dopants, in concentrations of up to 10^{-2} mole per silver mole and typically less than 10^{-4} mole per silver mole, can be present in the grains. Compounds of metals such as copper, thallium, lead, mercury, bismuth, zinc, cadmium, rhenium, and Group VIII metals (e.g., iron, ruthenium, rhodium, palladium, osmium, iridium, and platinum) can be present during grain precipitation, preferably during the growth stage of precipitation. The modification of photographic properties is related to the level and location of the dopant within the grains. When the metal forms a part of a coordination complex, such as a hexacoordination complex or a tetracoordination complex, the ligands can

also be included within the grains and the ligands can further influence photographic properties. Coordination ligands, such as halo, aquo, cyano cyanate, thiocyanate, nitrosyl, thionitrosyl, oxo and carbonyl ligands are contemplated and can be relied upon to modify photographic properties.

Dopants and their addition are illustrated by Arnold et al U.S. Patent 1,195,432; Hochstetter U.S. Patent 1,951,933; Trivelli et al U.S. Patent 2,448,060; Overman U.S. Patent 2,628,167; Mueller et al U.S. Patent 2,950,972; McBride U.S. Patent 3,287,136; Sidebotham U.S. Patent 3,488,709; Rosecrants et al U.S. Patent 3,737,313; Spence et al U.S. Patent 3,687,676; Gilman et al U.S. Patent 3,761,267; Shiba et al U.S. Patent 3,790,390; Ohkubo et al U.S. Patent 3,890,154; Iwaosa et al U.S. Patent 3,901,711; Habu et al U.S. Patent 4,173,483; Atwell U.S. Patent 4,269,927; Janusonis et al U.S. Patent 4,835,093; McDugle et al U.S. Patents 4,933,272, 4,981,781, and 5,037,732; Keevert et al U.S. Patent 4,945,035; and Evans et al U.S. Patent 5,024,931, the disclosures of which are here incorporated by reference. For background as to alternatives known to the art attention is directed to B. H. Carroll, "Iridium Sensitization: A Literature Review", *Photographic Science and Engineering*, Vol. 24, NO. 6, Nov./Dec. 1980, pp. 265-257, and Grzeskowiak et al published European Patent Application 0 264 288.

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

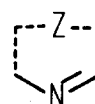
Although not essential to the practice of the invention, a further procedure that can be employed to maximize the population of tabular grains having {100} major faces is to incorporate an agent capable of restraining the emergence of non-{100} grain crystal faces in the emulsion during its preparation.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

Useful restraining agents under the contemplated conditions of precipitation are organic compounds containing a nitrogen atom with a resonance stabilized 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)

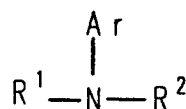


where

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

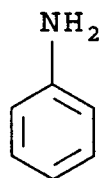
Ar is an aromatic ring structure containing from 5 to 14 carbon atoms and

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

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

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

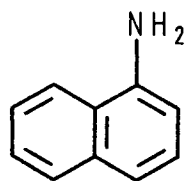
R-1



aniline

RA-2

5

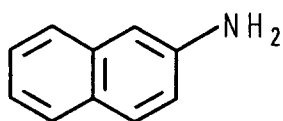


10

α -naphthylamine

RA-3

15

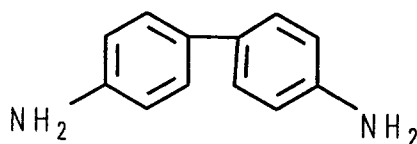


20

β -naphthylamine

RA-4

25

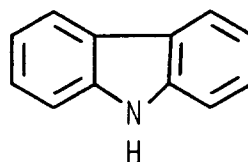


benzidine

30

RA-5

35

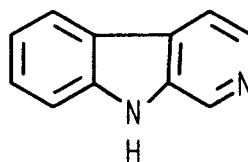


carbazole

40

RA-6

45



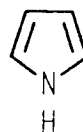
norharman

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RA-7

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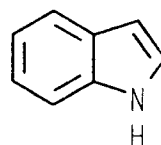


pyrrole

10

RA-8

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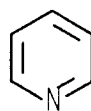


indole

20

RA-9

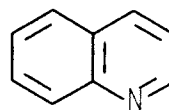
25



pyridine

RA-10

30

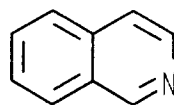


quinoline

35

RA-11

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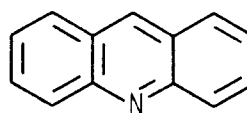


isoquinoline

45

RA-12

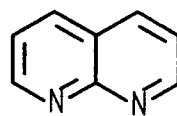
50



acridine

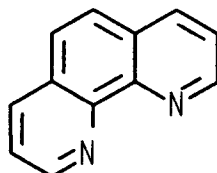
55

RA-13



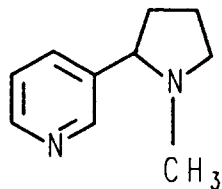
1,8-naphthyridine

RA-14



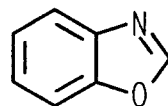
1,10-phenanthroline

RA-15



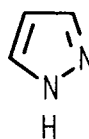
nicotine

RA-16



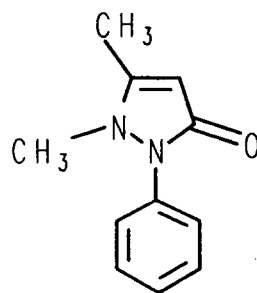
benzoxazole

RA-17



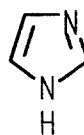
pyrazole

RA-18



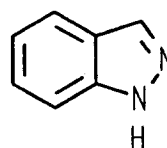
antipyrine

RA-19



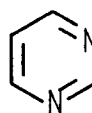
imidazole

RA-20



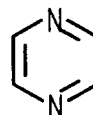
indazole

RA-21



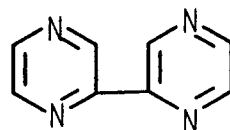
pyrimidine

RA-22



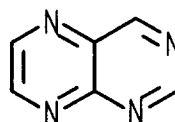
pyrazine

RA-23



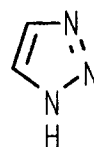
2,2'-bipyrazine

RA-24



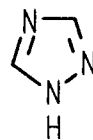
pteridine

RA-25



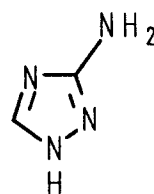
1,2,3-triazole

RA-26



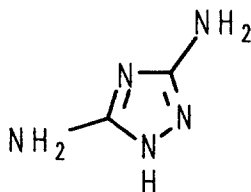
1,2,4-triazole

RA-27



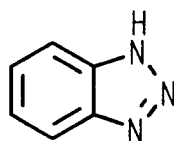
3-amino-1,2,4-triazole

RA-28



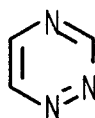
3,5-diamino-1,2,4-triazole

RA-29



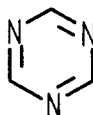
benzotriazole

RA-30



1,2,4-triazine

RA-31



1,3,5-triazine

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

It is specifically contemplated to deposit epitaxially silver salt onto the tabular grains acting as hosts. Conventional epitaxial depositions onto high chloride silver halide grains are illustrated by Maskasky U.S. Patent 4,435,501 (particularly Example 24B); Ogawa et al U.S. Patents 4,786,588 and 4,791,053; Hasebe et

al U.S. Patents 4,820,624 and 4,865,962; Sugimoto and Miyake, "Mechanism of Halide Conversion Process of Colloidal AgCl Microcrystals by Br⁻ Ions", Parts I and II, *Journal of Colloid and Interface Science*, Vol. 140, No. 2, Dec. 1990, pp. 335-361; Houle et al U.S. Patent 5,035,992; and Japanese published applications (Kokai) 252649-A (priority 02.03.90-JP 051165 Japan) and 288143-A (priority 04.04.90-JP 089380 Japan).

5 The disclosures of the above U.S. patents are here incorporated by reference.

The emulsions of the invention can be chemically sensitized with active gelatin as illustrated by T. H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, pp. 67-76, or with sulfur, selenium, tellurium, gold, platinum, palladium, iridium, osmium, rhenium or phosphorus sensitizers or combinations of these sensitizers, such as at pAg levels of from 5 to 10, pH levels of from 5 to 8 and
 10 temperatures of from 30 to 80 °C, as illustrated by *Research Disclosure*, Vol. 120, April, 1974, Item 12008, *Research Disclosure*, Vol. 134, June, 1975, Item 13452, Sheppard et al U.S. Patent 1,623,499, Matthies et al U.S. Patent 1,673,522, Waller et al U.S. Patent 2,399,083, Damschroder et al U.S. Patent 2,642,361, McVeigh U.S. Patent 3,297,447, Dunn U.S. Patent 3,297,446, McBride U.K. Patent 1,315,755, Berry et al U.S. Patent 3,772,031, Gilman et al U.S. Patent 3,761,267, Ohi et al U.S. Patent 3,857,711, Klinger et al U.S.
 15 Patent 3,565,633, Oftedahl U.S. Patents 3,901,714 and 3,904,415 and Simons U.K. Patent 1,396,696; chemical sensitization being optionally conducted in the presence of thiocyanate derivatives as described in Damschroder U.S. Patent 2,642,361; thioether compounds as disclosed in Lowe et al U.S. Patent 2,521,926, Williams et al U.S. Patent 3,021,215 and Bigelow U.S. Patent 4,054,457; and azaindenes, azapyridazines and azapyrimidines as described in Dostes U.S. Patent 3,411,914, Kuwabara et al U.S. Patent 3,554,757,
 20 Oguchi et al U.S. Patent 3,565,631 and Oftedahl U.S. Patent 3,901,714; elemental sulfur as described by Miyoshi et al European Patent Application EP 294,149 and Tanaka et al European Patent Application EP 297,804; and thiosulfonates as described by Nishikawa et al European Patent Application EP 293,917. Additionally or alternatively, the emulsions can be reduction-sensitized--e.g., with hydrogen, as illustrated by Janusonis U.S. Patent 3,891,446 and Babcock et al U.S. Patent 3,984,249, by low pAg (e.g., less than 5),
 25 high pH (e.g., greater than 8) treatment, or through the use of reducing agents such as stannous chloride, thiourea dioxide, polyamines and amineboranes as illustrated by Allen et al U.S. Patent 2,983,609, Oftedahl et al *Research Disclosure*, Vol. 136, August, 1975, Item 13654, Lowe et al U.S. Patents 2,518,698 and 2,739,060, Roberts et al U.S. Patents 2,743,182 and '183, Chambers et al U.S. Patent 3,026,203 and Bigelow et al U.S. Patent 3,361,564.

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

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

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

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

One or more spectral sensitizing dyes may be employed. Dyes with sensitizing maxima at wavelengths throughout the visible and infrared spectrum and with a great variety of spectral sensitivity curve shapes are known. The choice and relative proportions of dyes depends upon the region of the spectrum to which sensitivity is desired and upon the shape of the spectral sensitivity curve desired. Dyes with overlapping spectral sensitivity curves will often yield in combination a curve in which the sensitivity at each wavelength in the area of overlap is approximately equal to the sum of the sensitivities of the individual dyes. Thus, it is possible to use combinations of dyes with different maxima to achieve a spectral sensitivity curve with a maximum intermediate to the sensitizing maxima of the individual dyes.

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

Spectral sensitizing dyes can also affect the emulsions in other ways. For example, spectrally sensitizing dyes can increase photographic speed within the spectral region of inherent sensitivity. Spectral sensitizing dyes can also function as antifoggants or stabilizers, development accelerators or inhibitors, reducing or nucleating agents, and halogen acceptors or electron acceptors, as disclosed in Brooker et al U.S. Patent 2,131,038, Illingsworth et al U.S. Patent 3,501,310, Webster et al U.S. Patent 3,630,749, Spence et al U.S. Patent 3,718,470 and Shiba et al U.S. Patent 3,930,860.

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

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

The following illustrate specific spectral sensitizing dye selections:

SS-1

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

SS-2

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

- SS-3
Anhydro-4,5-benzo-3'-methyl-4'-phenyl-1-(3-sulfopropyl)naphtho[1,2-d]thiazolothiazolocyanine hydroxide
- SS-4
1,1'-Diethylnaphtho[1,2-d]thiazolo-2'-cyanine bromide
- 5 SS-5
Anhydro-1,1'-dimethyl-5,5'-di-(trifluoromethyl)-3-(4-sulfobutyl)-3'-(2,2,2-trifluoroethyl)-benzimidazolocarbocyanine hydroxide
- SS-6
Anhydro-3,3'-(2-methoxyethyl)-5,5'-diphenyl-9-ethyloxacarbocyanine, sodium salt
- 10 SS-7
Anhydro-11-ethyl-1,1'-di-(3-sulfopropyl)naphtho[1,2-d]oxazolocarbocyanine hydroxide, sodium salt
- SS-8
Anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)oxaselenacarbocyanine hydroxide, sodium salt
- SS-9
5,6-Dichloro-3',3'-dimethyl-1,1',3-triethylbenzimidazolo-3H-indolocarbocyanine bromide
- 15 SS-10
Anhydro-5,6-dichloro-1,1-diethyl-3-(3-sulfopropyl)benzimidazoloacarbocyanine hydroxide
- SS-11
Anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(2-sulfoethylcarbamoylmethyl)thiacarbocyanine hydroxide, sodium salt
- 20 SS-12
Anhydro-5',6'-dimethoxy-9-ethyl-5-phenyl-3-(3-sulfobutyl)-3'-(3-sulfopropyl)oxathiacarbocyanine hydroxide, sodium salt
- SS-13
Anhydro-5,5'-dichloro-9-ethyl-3-(3-phosphonopropyl)-3'-(3-sulfopropyl)thiacarbocyanine hydroxide
- 25 SS-14
Anhydro-3,3'-di-(2-carboxyethyl)-5,5'-dichloro-9-ethylthiacarbocyanine bromide
- SS-15
Anhydro-5,5'-dichloro-3-(2-carboxyethyl)-3'-(3-sulfopropyl)thiacyanine sodium salt
- 30 SS-16
9-(5-Barbituric acid)-3,5-dimethyl-3'-ethyltellurathiacarbocyanine bromide
- SS-17
Anhydro-5,6-methylenedioxy-9-ethyl-3-methyl-3'-(3-sulfopropyl)tellurathiacarbocyanine hydroxide
- SS-18
3-Ethyl-6,6'-dimethyl-3'-pentyl-9.11-neopentyleneethiadibenzocyanine bromide
- 35 SS-19
Anhydro-3-ethyl-9,11-neopentylene-3'-(3-sulfopropyl)thiadibenzocyanine hydroxide
- SS-20
Anhydro-3-ethyl-11,13-neopentylene-3'-(3-sulfopropyl)oxathiatricarbocyanine hydroxide, sodium salt
- 40 SS-21
Anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt
- SS-22
Anhydro-5,5'-diphenyl-3,3'-di-(3-sulfobutyl)-9-ethyloxacarbocyanine hydroxide, sodium salt
- 45 SS-23
Anhydro-5,5'-dichloro-3,3'-di-(3-sulfopropyl)-9-ethylthiacarbocyaninehydroxide, triethylammonium salt
- SS-24
Anhydro-5,5'-dimethyl-3,3'-di-(3-sulfopropyl)-9-ethylthiacarbocyaninehydroxide, sodium salt
- SS-25
Anhydro-5,6-dichloro-1-ethyl-3-(3-sulfobutyl)-1'-(3-sulfopropyl)benzimidazonaphtho[1,2-d]-thiazolocarbocyanine hydroxide, triethylammonium salt
- 50 SS-26
Anhydro-11-ethyl-1,1'-di-(3-sulfopropyl)naphth[1,2-d]oxazolocarbocyanine hydroxide, sodium salt
- SS-27
Anhydro-3,9-diethyl-3'-methylsulfonylcarbamoylmethyl-5-phenyloxathiacarbocyanine *p*-toluenesulfonate
- 55 SS-28
Anhydro-6,6'-dichloro-1,1'-diethyl-3,3'-di-(3-sulfopropyl)-5,5'-bis(trifluoromethyl)-benzimidazolocarbocyanine hydroxide, sodium salt

SS-29

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

SS-30

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

SS-31

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

SS-32

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

SS-33

4-[2-((1,4-Dihydro-1-dodecylpyridin-ylidene)ethylidene)-3-phenyl-2-isoxazolin-5-one

SS-34

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

SS-35

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

SS-36

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

SS-37

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

SS-38

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

SS-39

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

SS-40

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

SS-41

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

SS-42

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

SS-43

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

SS-44

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

SS-45

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

SS-46

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

SS-47

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

SS-48

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

SS-49

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

SS-50

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

SS-51

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

Instability which increases minimum density in negative-type emulsion coatings (i.e., fog) can be protected against by incorporation of stabilizers, antifoggants, antikinking agents, latent-image stabilizers and similar addenda in the emulsion and contiguous layers prior to coating. Most of the antifoggants effective in the emulsions of this invention can also be used in developers and can be classified under a

few general headings, as illustrated by C.E.K. Mees, *The Theory of the Photographic Process*, 2Nd Ed., Macmillan, 1954, pp. 677-680.

To avoid such instability in emulsion coatings, stabilizers and antifoggants can be employed, such as halide ions (e.g., bromide salts); chloropalladates and chloropalladites as illustrated by Trivelli et al U.S. Patent 2,566,263; water-soluble inorganic salts of magnesium, calcium, cadmium, cobalt, manganese and zinc as illustrated by Jones U.S. Patent 2,839,405 and Sidebotham U.S. Patent 3,488,709; mercury salts as illustrated by Allen et al U.S. Patent 2,728,663; selenols and diselenides as illustrated by Brown et al U.K. Patent 1,336,570 and Pollet et al U.K. Patent 1,282,303; quaternary ammonium salts of the type illustrated by Allen et al U.S. Patent 2,694,716, Brooker et al U.S. Patent 2,131,038, Graham U.S. Patent 3,342,596 and Arai et al U.S. Patent 3,954,478; azomethine desensitizing dyes as illustrated by Thiers et al U.S. Patent 3,630,744; isothioureas derivatives as illustrated by Herz et al U.S. Patent 3,220,839 and Knott et al U.S. Patent 2,514,650; thiazolidines as illustrated by Scavron U.S. Patent 3,565,625; peptide derivatives as illustrated by Maffet U.S. Patent 3,274,002; pyrimidines and 3-pyrazolidones as illustrated by Welsh U.S. Patent 3,161,515 and Hood et al U.S. Patent 2,751,297; azotriazoles and azotetrazoles as illustrated by Baldassarri et al U.S. Patent 3,925,086; azaindenes, particularly tetraazaindenes, as illustrated by Heimbach U.S. Patent 2,444,605, Knott U.S. Patent 2,933,388, Williams U.S. Patent 3,202,512, *Research Disclosure*, Vol. 134, June, 1975, Item 13452, and Vol. 148, August, 1976, Item 14851, and Nepker et al U.K. Patent 1,338,567; mercaptotetrazoles, - triazoles and -diazoles as illustrated by Kendall et al U.S. Patent 2,403,927, Kennard et al U.S. Patent 3,266,897, *Research Disclosure*, Vol. 116, December, 1973, Item 11684, Luckey et al U.S. Patent 3,397,987 and Salesin U.S. Patent 3,708,303; azoles as illustrated by Peterson et al U.S. Patent 2,271,229 and *Research Disclosure*, Item 11684, cited above; purines as illustrated by Sheppard et al U.S. Patent 2,319,090, Birr et al U.S. Patent 2,152,460, *Research Disclosure*, Item 13452, cited above, and Dostes et al French Patent 2,296,204, polymers of 1,3-dihydroxy(and/or 1,3-carbamoxy)-2-methylenepropane as illustrated by Saleck et al U.S. Patent 3,926,635 and tellurazoles, tellurazolines, tellurazolinium salts and tellurazolium salts as illustrated by Gunther et al U.S. Patent 4,661,438, aromatic oxatellurazolinium salts as illustrated by Gunther, U.S. Patent 4,581,330 and Przyklek-Elling et al U.S. Patents 4,661,438 and 4,677,202. High-chloride emulsions can be stabilized by the presence, especially during chemical sensitization, of elemental sulfur as described by Miyoshi et al European published Patent Application EP 294,149 and Tanaka et al European published Patent Application EP 297,804 and thiosulfonates as described by Nishikawa et al European published Patent Application EP 293,917.

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

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

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

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

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

Among stabilizers useful in protecting emulsion layers against development fog are addenda such as azabenzimidazoles as illustrated by Bloom et al U.K. Patent 1,356,142 and U.S. Patent 3,575,699, Rogers U.S. Patent 3,473,924 and Carlson et al U.S. Patent 3,649,267; substituted benzimidazoles, benzothiazoles,

benzotriazoles and the like as illustrated by Brooker et al U.S. Patent 2,131,038, Land U.S. Patent 2,704,721, Rogers et al U.S. Patent 3,265,498; mercapto-substituted compounds, e.g., mercaptotetrazoles, as illustrated by Dimsdale et al U.S. Patent 2,432,864, Rauch et al U.S. Patent 3,081,170, Weyerts et al U.S. Patent 3,260,597, Grasshoff et al U.S. Patent 3,674,478 and Arond U.S. Patent 3,706,557; isothiurea derivatives as illustrated by Herz et al U.S. Patent 3,220,839, and thiodiazole derivatives as illustrated by von Konig U.S. Patent 3,364,028 and von Konig et al U.K. Patent 1,186,441.

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

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

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

Where the photographic element is to be processed at elevated bath or drying temperatures, as in rapid access processors, pressure desensitization and/or increased fog can be controlled by selected combinations of addenda, vehicles, hardeners and/or processing conditions as illustrated by Abbott et al U.S. Patent 3,295,976, Barnes et al U.S. Patent 3,545,971, Salesin U.S. Patent 3,708,303, Yamamoto et al U.S. Patent 3,615,619, Brown et al U.S. Patent 3,623,873, Taber U.S. Patent 3,671,258, Abele U.S. Patent 3,791,830, *Research Disclosure*, Vol. 99, July, 1972, Item 9930, Florens et al U.S. Patent 3,843,364, Priem et al U.S. Patent 3,867,152, Adachi et al U.S. Patent 3,967,965 and Mikawa et al U.S. Patents 3,947,274 and 3,954,474.

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

Apart from the features that have been specifically discussed the tabular grain emulsion preparation procedures, the tabular grains that they produce, and their further use in photography can take any convenient conventional form. Substitution for conventional emulsions of the same or similar silver halide composition is generally contemplated, with substitution for silver halide emulsions of differing halide composition, particularly tabular grain emulsions, being also feasible in many types of photographic applications. The low levels of native blue sensitivity of the high chloride {100} tabular grain emulsions of the invention allows the emulsions to be employed in any desired layer order arrangement in multicolor photographic elements, including any of the layer order arrangements disclosed by Kofron et al U.S. Patent

4,439,520, the disclosure of which is here incorporated by reference, both for layer order arrangements and for other conventional features of photographic elements containing tabular grain emulsions. Conventional features are further illustrated by the following incorporated by reference disclosures:

- ICBR-1 *Research Disclosure*, Vol. 308, December 1989, Item 308,119;
- 5 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;
- 10 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;
- 15 ICBR-12 Ikeda et al U.S. Patent 4,806,461, issued Feb. 21, 1989;
- ICBR-13 Makino et al U.S. Patent 4,853,322, issued Aug. 1, 1989; and
- ICBR-14 Daubendiek et al U.S. Patent 4,914,014, issued Apr. 3, 1990.

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

30 Examples

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

40 Emulsions A-K (Comparative)

These examples demonstrate repeated attempts to form {100} tabular grain emulsions following the teachings of Bogg U.S. Patent 4,063,951. Since the only Example provided by Bogg was directed to a silver iodobromide emulsion, the first emulsion preparations also used iodide and bromide salts. In subsequent preparation attempts chloride and iodochloride emulsion preparations were attempted.

45 Emulsion A

A 2000 mL solution containing 5.0% by weight bone gelatin and 0.2 mL of tributylphosphate anti-foamant was provided in a reaction vessel at 65 °C, stirred with a highly pitched, 7.6 cm diameter, three-blade marine propeller at 250 rpm. The initial pH was 5.74. While the solution was stirred, a 4.7 M silver nitrate solution and a 4.465 M ammonium bromide and 0.235 M ammonium iodide solution were added simultaneously at 21.2 mL/min for 22.2 minutes with the pAg controlled at 6.0. The temperature was then reduced to 45 °C linearly over 10 minutes. After the temperature was reduced, 147 mL of an 11.8 M ammonium hydroxide solution were rapidly added and the mixture was held for 10 minutes. The pBr was 3.25 after the ammonia was added.

The resulting emulsion contained relatively polydisperse cubic grains with rounded corners. Out of 672 grains observed on a scanning electron microscope (SEM) at a magnification of 20,000 X, 21 grains (3%) showed a slight rectangular shape with a ratio of adjacent edge lengths of less than 1.3 and typically 1.1.

SEM observations of grains tilted so that the thickness could be observed showed that the few grains present that appeared rectangular exhibited aspect ratios of less than 2.

Emulsion B

5

The precipitation process was the same as that used for Emulsion A, except that mixing was improved by increasing the rpm of the marine propeller to 600 and the latitude of pAg variation during the preparation more restricted with the pAg being centered at 7.7. The pBr after the ammonium hydroxide was added was 2.7.

10 The resulting emulsion contained polydisperse spherical grains of about 0.5 μm in ECD, showing {111} (i.e., octahedral) crystal faces.

Emulsion C

15 The precipitation process was the same as that used for Emulsion A, except that the marine propeller was replaced by a high rpm mixing device operating at 5000 rpm. The range of pAg variance restricted to the range of 5.7 to 6.5 and was centered at a pAg of 6.1. The pBr after the addition of the ammonium hydroxide was 2.7.

20 The resulting emulsion contained polydisperse spherical grains with an average ECD of about 0.5 μm , showing (111) faces.

Emulsion D

25 The precipitation process was the same as that used for Emulsion B, except that immediately after the addition of the ammonium hydroxide, 18.1 mL of 4.7 M silver nitrate was added to reduce excess halide and increase the pBr to 3.5 during the 10 minute ripening period.

A sample of the emulsion taken before the temperature was reduced to 45 °C showed a relatively monodisperse population of cubes with an edge length of about 0.2 μm , similar to that described by Bogg.

30 After the 10 minute ripening period the emulsion appeared essentially similar to Emulsion A, being composed of almost entirely cubic grains with a small percentage of the grains showing a rectangular shape and an aspect ratio less than 2.

Emulsion E

35 The precipitation process was the same as that used for Emulsion D, except that 39.5 mL of 4.7 M silver nitrate were added immediately after the addition of the ammonium hydroxide to further reduce the excess halide and raise the pBr to 3.95 during the 10 minute ripening period.

The resulting emulsion appeared similar to Emulsion D.

Emulsion F

The precipitation process was the same as that used for Emulsion D, except that 115 mL of 4.7 M silver nitrate were added immediately after the addition of the ammonium hydroxide to raise the pBr to 5.0 during the 10 minute ripening period.

45 The resulting emulsion again appeared similar to Emulsion D.

Emulsion G

50 The precipitation process was the same as that used for Emulsion D, except that 142 mL of 4.7 M silver nitrate were added immediately after the addition of the ammonium hydroxide to raise the pBr to 6.1 during the 10 minute ripening period.

The resulting emulsion again appeared similar to Emulsion D.

Emulsion H

55

The precipitation process was the same as that used for Emulsion F, except that the iodide content in the salt solution was reduced by a factor of 10 by using a solution composed of 4.6765 M ammonium bromide and 0.0235 M ammonium iodide. The amount of 4.7 M silver nitrate added after the ammonium

hydroxide addition was increased slightly to 124 mL and the pBr was 5.4.

The resulting emulsion again appeared similar to Emulsions D through G.

Emulsion I

The precipitation process was the same as that used for Emulsion H, except that the amount of silver nitrate added after the ammonium hydroxide dump was 9 mL to adjust the pBr to 3.25 during the 10 minute ripening period.

The resulting emulsion again looked about identical to Emulsions D through H.

Emulsions A and D through H most closely resembled the grain shapes disclosed by Bogg U.S. Patent 4,063,951, but with two differences: (1) the percentage of rectangular grains was much lower in the Emulsions above and (2) the average grain diameter was about 0.3 μm . It was not apparent how a silver iodobromide emulsion could be prepared having the grain population disclosed by Bogg using a precipitation procedure of the type taught by Bogg.

The following two emulsions show the results obtained when ammonium bromide was replaced by ammonium chloride.

Example J

The precipitation process was the same as that used for Emulsion A, except that the ammonium bromide and ammonium iodide solutions were replaced with an equimolar amount of ammonium chloride. The pCl during the ripening period was 1.5. No iodide was added.

The resulting emulsion was composed of a wide variety of polymorphic, very low aspect ratio grains showing a variety of crystal faces including {111} faces. A very small number of the grains were square or rectangular, but exhibited aspect ratios of less than 2. The corners of every grain had been modified and showed both {111} and {110} crystal faces. The mean grain ECD was much larger than that of the previous emulsions at about 10 μm .

Emulsion K

This emulsion was prepared identically to Example J, except that ammonium iodide was added to the salt solution such that the composition was 4.465 M ammonium chloride and 0.265 M ammonium iodide. The pCl during the 10 minute ripening period was 1.6.

The resulting emulsion appeared almost identical to the bromide Emulsions A and D through H, except that most of the emulsion grains had modified corners exhibiting {111} or {110} crystallographic faces. The mean grain ECD was also less than 0.5 μm , as was observed in the bromide examples. This silver iodochloriodide emulsion also contained a low percentage of grains that were slightly rectangular, but the rectangular grains exhibited an aspect ratio of less than 2. As in Emulsion J, most of the corners of the grains were modified and showed {111} faces.

Based on these investigations it was concluded that a tabular grain emulsion satisfying the requirements of this invention could not be prepared by following the teachings of Bogg U.S. Patent 4,063,951.

Example 1

A 6090 mL solution containing 3.52% by weight of low methionine gelatin, 0.0056 M sodium chloride and 1.48×10^{-4} potassium iodide was provided in a stirred reaction vessel at 40 °C. While the solution was vigorously stirred, 90 mL of 2.0 M silver nitrate and 90 mL of a 1.99 M sodium chloride and 0.01 M potassium iodide solution were added simultaneously at a rate of 180 mL/min each. The mixture was then held for 10 minutes with the temperature remaining at 40 °C. Following the hold, a 1.0 M silver nitrate solution and a 1.0 M sodium chloride solution were added simultaneously at 12 mL/min for 40 minutes followed by a linear acceleration from 12 mL/min to 33.7 mL/min over 233.2 minutes, while maintaining the pCl at 2.25. The pCl was then adjusted to 1.30 with sodium chloride then washed using ultrafiltration to a pCl of 2.0 then adjusted to a pCl of 1.65 with sodium chloride. The resulting emulsion was a tabular grain silver iodochloride emulsion contained 0.03 mole percent iodide with a mean equivalent circular grain diameter of 1.51 μm and a mean thickness of 0.22 μm . Greater than 50 percent of total grain projected area was accounted for by {100} tabular grains exhibiting an average aspect ratio of 6.9.

Example 2

A 1536 mL solution containing 3.52% by weight of low methionine (hydrogen peroxide treated) gelatin, 0.0056 M sodium chloride, 2.34×10^{-4} M potassium iodide, and 0.3 mL of a polyethylene glycol antifoamant was provided in a stirred reaction vessel at 40 °C. While the solution was vigorously stirred, 30 mL of 2.0 M silver nitrate and 30 mL of a 2.0 M sodium chloride solution were added simultaneously at a rate of 60 mL/min each. The mixture was then held for 10 seconds. Following the hold, a 0.5 M silver nitrate solution and a 0.5 M sodium chloride solution were added simultaneously at 8 mL/min for 40 minutes with the pCl maintained at 2.35. The pCl was then adjusted to 1.65 with 1.0 M sodium chloride. The 0.5 M silver nitrate and the 0.5 M sodium chloride were then each added at a linearly increasing the flow rate, commencing at 8 mL/min and increasing at a rate of 0.0615 mL/min while maintaining pCl at 1.65. After 90 minutes microscopic observation of the emulsion showed an equivalent circular diameter of 0.9 μm with a mean grain thickness of 0.17 μm . Greater than 50 percent of total grain projected area was accounted for by {100} tabular grains exhibiting an average aspect ratio of 5.3.

Example 3

A 1.5 L solution containing 3.52% by weight of low methionine gelatin, 0.0056 M sodium chloride and 0.2 mL of polyethylene glycol antifoamant provided in a stirred reaction vessel at 40 °C. While the solution was vigorously stirred, 45 mL of a 0.01 M potassium iodide solution were added, followed by 50 mL of 1.25 M silver nitrate and 50 mL of a 1.25M sodium chloride solution, added simultaneously each at a rate of 100 mL/min. The mixture was then held for 10 seconds with the temperature remaining at 40 °C. Following the hold, a 0.625 M silver nitrate solution containing 0.08 mg mercuric chloride per mole of silver nitrate and a 0.625 M sodium chloride solution were added simultaneously each at 10 mL/min for 30 minutes while the pCl was maintained at 2.35. The reaction vessel pCL was then adjusted to 1.25 by adding 2 M sodium chloride over 1 minute. This was followed by a linearly accelerated simultaneous addition of 0.625 M silver nitrate and 0.625 M sodium chloride solutions, each at a rate of from 10 mL/min to 15 mL/min over 125 minutes, then at a constant flow rate for 30 minutes each a rate of 15 mL/min while maintaining the pCl at 1.25. Forty grams of phthalated gelatin were added, and the emulsion was washed and concentrated using procedures of Yutzy et al U.S. Patent 2,614,918. The pCl after washing was 2.0. Twenty-one grams of low methionine gel were added, the pCl was adjusted to 1.65 with sodium chloride, and the pH was adjusted to 5.7. The resulting emulsion was a silver iodochloride {100} tabular grain emulsion containing 0.036 mole percent iodide. More than 90 percent of total grain projected area was accounted for by grains with rectangular {100} major faces and sharp unmodified corners. The emulsion had a mean ECD of 0.89 μm and a mean grain thickness of 0.34 μm .

Example 4

This emulsion was precipitated and washed identically to the emulsion of Example 3, except the pCl during the accelerated and final growth segments was maintained at 1.65. Approximately 90 percent of total grain projected area was accounted for by square and rectangular grains with {100} major faces. The mean ECD of the emulsion grains was 1.08 μm , and their average thickness was 0.25 μm .

Emulsion L (comparative)

This emulsion was prepared to provide a silver chloride {100} cubic grain emulsion with a mean grain volume matching that of the emulsion of Example 3, to thereby allow the photographic response of the emulsions to be easily compared.

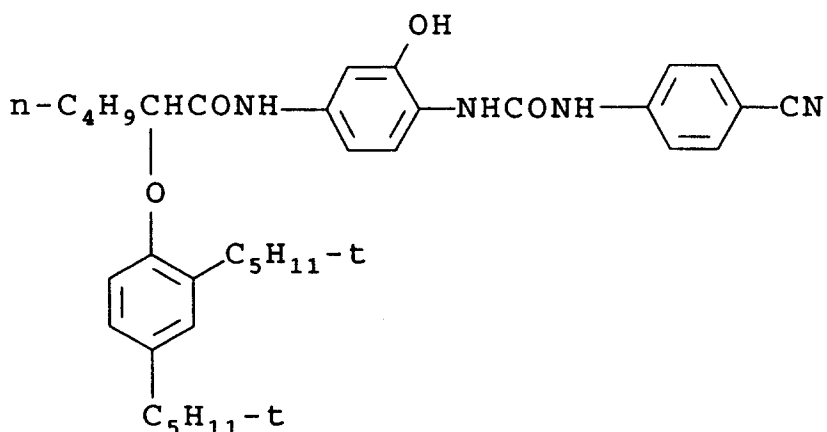
A 5.0 L solution containing 8.0% by weight of low methionine gelatin, 0.026 M sodium chloride and 1.0 ml of ethylene oxide/propylene oxide block copolymer antifoamant provided in a stirred reaction vessel at 65 °C. While the solution was vigorously stirred, a 4.0 M silver nitrate solution containing 0.08 mg of mercuric chloride per mole of silver nitrate and a 4.0 M sodium chloride solution were simultaneously added at a rate of 18 mL/min each for 1 minute with the pCl controlled at 1.6. Over the next 20 minutes, the flow rates of the silver nitrate and salt solution were increased from 18 to 80 mL/min, then the flow rates were held constant at 80 mL/min for 65 minutes with the pCl controlled at 1.6. The emulsion was then washed and concentrated by ultrafiltration. Low methionine gelatin in the amount of 560 g was added, and pCl was adjusted to 1.6 with a sodium chloride solution. The resulting cubic grain emulsion had a mean cubic grain edge length of 0.6 μm .

Example 5

The Example 3 emulsion and Emulsion L were similarly sensitized, coated and photographically evaluated.

To identify empirically a substantially optimum sensitization samples of each emulsion were sensitized by varying the concentrations added of spectral sensitizing dye, sulfur sensitizers and gold sensitizers as well as the elevated temperature hold (digestion) times following addition of sensitizers. The general sensitization procedure was as follows: An emulsion sample was melted at 40 °C, with 1200 mg/mole of potassium bromide added to the samples. Green spectral sensitizing dye SS-21 was then added, followed by a 20 minute hold. This was followed by the addition of sodium thiosulfate pentahydrate, then potassium tetrachloroaurate. The temperature of the well stirred mixture was then raised to 60 °C over 12 minutes and held at 60 °C for 10 minutes. The emulsion was rapidly cooled to 40 °C, 70 mg/mole of APMT was added, and the emulsion was chill set.

Each sample was coated on a support provided with an antihalation layer at 0.85 g/m² of silver with 1.08 g/m² of cyan dye-forming coupler C and 2.7 g/m² of gelatin. This layer was overcoated with 1.6 g/m² of gelatin, and the entire coating was hardened with bis(vinylsulfonylmethyl)ether at 1.75% of the total coated gelatin. Coatings were exposed through a step wedge for 0.02 second with a 3000 °K tungsten source filtered with a Daylight V and a Kodak Wratten TM 9 filter. The coatings were processed in the Kodak Flexicolor TM C-41 process.

Coupler C

The photographic performance of the samples of Emulsion L and the emulsion of Example 3 having substantially matched acceptable minimum densities and the highest attainable sensitivity (i.e., substantially optimally sensitized samples) were as follows:

Emulsion L exhibited a minimum density of 0.23. It was assigned a relative sensitivity of 100. Its contrast normalized granularity was 0.018.

The Example 3 emulsion exhibited a minimum density of 0.22. Its relative sensitivity was 178. Its contrast normalized granularity was 0.019. A large sensitivity advantage was exhibited by the Example 3 emulsion. Although the Example 3 emulsion and Emulsion L exhibited a small difference in their granularities, the large sensitivity difference more than offset the granularity differences. From the data it is apparent the Example 3 emulsion would exhibit a large sensitivity advantage versus a cubic grain emulsion of matched granularity.

Emulsion M

This emulsion preparation demonstrates the inability of a ripening out procedure--specifically the procedure referred to in the 1963 Torino Symposium, cited above--to produce a tabular grain emulsion satisfying the requirements of the invention.

To a reaction vessel containing 75 mL distilled water, 6.75 g deionized bone gelatin and 2.25 mL of 1.0 M NaCl solution at 40 °C were simultaneously added with efficient stirring 15 mL of 1.0 M AgNO₃ solution and 15 mL of 1.0 M NaCl solution each at 15 mL per minute. The mixture was stirred at 40 °C for 4

minutes, then the temperature was increased to 77 °C over a period of 10 minutes and 7.2 mL of 1.0 M NaCl solution were added. The mixture was stirred at 77 °C for 180 minutes and then cooled to 40 °C.

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

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

Claims

1. A radiation sensitive emulsion comprised of a dispersing medium and silver halide grains, characterized in that at least 50 percent of total grain projected area is accounted for by tabular grains
 - (1) bounded by {100} major faces having adjacent edge ratios of less than 10,
 - (2) each having an aspect ratio of at least 2 and together having an average aspect ratio of up to 8, and
 - (3) internally at their nucleation site containing iodide and at least 50 mole percent chloride.
2. A radiation sensitive emulsion according to claim 1 further characterized in that the tabular grains have an average aspect ratio of at least 5.
3. A radiation sensitive emulsion according to claim 1 or 2 further characterized in that the tabular grains have adjacent major face edge ratios of less than 5.
4. A radiation sensitive emulsion according to claim 3 further characterized in that the tabular grains have adjacent major face edge ratios of less than 2.
5. A radiation sensitive emulsion according to any one of claims 1 to 4 inclusive further characterized in that the tabular grains have thicknesses of less than 0.8 μm .
6. A radiation sensitive emulsion according to claim 5 further characterized in that the tabular grains are thin tabular grains having thicknesses of less than 0.3 μm .
7. A radiation sensitive emulsion according to any one of claims 1 to 6 inclusive further characterized in that the tabular grains contain at least 70 mole percent chloride.
8. A radiation sensitive emulsion according to claim 7 further characterized in that the tabular grains contain at least 90 mole percent chloride.
9. A radiation sensitive emulsion according to claim 8 further characterized in that the tabular grains are silver iodochloride grains.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 4416

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)
A	US-A-4 425 426 (T.I.ABBOTT, C.G.JONES) * column 10, line 53 - line 68; claims 1-15 * ---	1-9	G03C1/005
A	GB-A-2 109 578 (EASTMAN KODAK COMPANY) * the whole document * ---	1-9	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 169 (P-1032) (4112) 30 March 1990 & JP-A-02 024 643 (FUJI PHOTO FILM COMPANY LTD.) 26 January 1990 * abstract * & WPI(Derwent) Access-no. 90-071406 ---	1-9	
D,A	US-A-4 063 951 (T.G.BOGG) * column 2, line 63 - line 68 * ---	1-9	
P,A, L	EP-A-0 534 395 (EASTMAN KODAK COMPANY) * the whole document * ---	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.5)
P,A	EP-A-0 584 644 (FUJI PHOTO FILM COMPANY LTD.) * example 2 * -----	1-9	G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 July 1994	Examiner Buscha, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			