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(54) **High edge cubicity tabular grain emulsion.**

(57) Tabular grain silver bromide and silver bromiodide emulsions are disclosed in which less than 75 percent of the edge surfaces joining the opposed parallel major octahedral grain faces of the tabular grains lie in {111} crystallographic planes. By increasing the edge cubicity (the proportion of the edge surfaces lying in non-{111} crystallographic planes) of the tabular grains the photographic properties of the emulsion are improved. The grains are in one form doped with iron and cyano ligands.

EP 0 515 894 A1

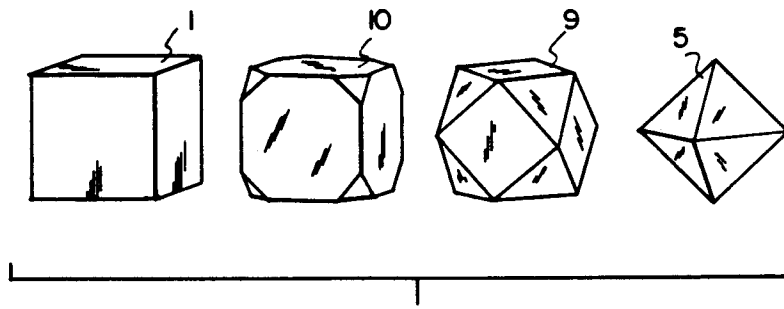


FIG. 7

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

Brief Description of the Drawings

Figure 1 is an isometric view of a regular cubic silver halide grain.

Figure 2 is a schematic diagram of the atomic arrangement at a silver bromide cubic crystal face.

Figure 3 is an isometric view of a regular octahedral silver halide grain.

Figure 4 is a schematic diagram of the interim atomic arrangement at a silver bromide octahedral crystal face.

Figure 5 is an isometric view of a regular rhombic dodecahedron.

Figure 6 is a schematic diagram of the atomic arrangement at a silver bromide rhombic dodecahedral crystal face.

Figure 7 is an isometric view of a regular cubic silver halide grain, a regular octahedral silver halide grain, and intermediate cubo-octahedral silver halide grains.

Silver halide photography has been practiced for more than a century. The radiation sensitive silver halide compositions initially employed for imaging were termed emulsions, since it was not originally appreciated that a solid phase was present. The term "photographic emulsion" has remained in use, although it has long been known that the radiation sensitive component is present in the form of dispersed microcrystals, typically referred to as grains.

Over the years silver halide grains have been the subject of intense investigation. Except for seldom employed high iodide silver halide grains, those containing at least 90 mole percent iodide based on silver, the silver halide grains used in photography exhibit a cubic crystal lattice structure. While silver chloride and silver chlorobromide grains are known and employed for selected photographic applications, in practice silver bromide crystal structures are most extensively employed, since they are capable of realizing high photographic speeds. The incorporation of a minor proportion of iodide ions within the silver bromide crystal structure undertaken to further enhance photographic speeds. While the iodide content of silver bromiodide grains can range up to about 40 mole percent, based on silver, depending on the temperature of precipitation, in practice, silver bromiodide emulsions typically contain less than 20 mole percent iodide.

The cubic crystal lattice silver bromide and bromiodide grains exhibit a variety of regular and irregular grain shapes. Apart from varied degrees of corner and edge rounding, the grains are polyhedral, being bounded by distinct crystal faces. These crystal faces can take any one of seven (7) known crystallographic forms:

(1) *The Cubic or {100} Form* Cubic crystal lattice silver halide favors the formation of crystallographic faces of either the cubic or octahedral form. Silver chloride strongly favors the formation of cubic crystal faces. Silver bromide also forms cubic crystal faces, but favors the formation of octahedral crystal faces in the presence of an excess of bromide ions. Iodide ions in the crystal structure tend to increase the grain preference for crystal faces of the octahedral form. A discussion of the factors which cause one crystallographic form to be favored over another is offered by James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, New York, 1977, PP. 98-101.

Regular silver halide grains bounded by cubic crystal faces are cubic in appearance when examined by electron microscopy. A regular cubic grain 1 is shown in Figure 1. The cubic grain is bounded by six identical crystal faces. In the photographic literature these crystal faces are usually referred to as {100} crystal faces, referring to the Miller index employed for designating crystal faces. While the {100} crystal face designation is most commonly employed in connection with silver halide grains, these same crystal faces are sometimes also referred to as {200} crystal faces, the difference in designation resulting from a difference in the definition of the basic unit of the crystal structure. Although the cubic crystal shape is readily visually identified in regular grains, in irregular grains the presence of cubic crystal faces is not always visually identifiable.

The practical importance of cubic crystal faces is the surface arrangement of silver and halide ions, which in turn influences the grain surface reactions and adsorptions typically encountered in photographic applications. A cubic {100} crystal plane surface arrangement of ions as theoretically hypothesized is schematically illustrated by Figure 2, wherein the smaller spheres 2 represent silver ions while the larger spheres 3 designate bromide ions. Although on an enlarged scale, the relative size and position of the silver and bromide ions is accurately represented. It can be seen that a plurality of parallel rows, indicated by lines 4, are present, each formed by alternating silver and bromide ions. In Figure 2 a portion of the next tier of ions lying below the surface tier is shown to illustrate their relationship to the surface tier of ions.

(2) *The Octahedral or {111} Form* In another form regular silver halide grains when observed by electron microscopy are octahedral in appearance. A regular octahedral grain 5 is shown in Figure 3. The octahedral grain is bounded by eight identical crystal faces. These crystal faces are referred to as octahedral or {111} crystal faces. Although the octahedral crystal shape is readily visually identified in regular grains, in irregular grains the presence of octahedral crystal faces is not always visually identifiable.

The basic difference between cubic {100} and octahedral {111} crystal faces can be appreciated by comparing Figures 2 and 4. The {100} crystal face presented by the uppermost tier of ions in Figure 2 consists of equal numbers of silver and bromide ions, as does the tier of ions immediately beneath the surface tier. In forming {111} crystal faces successive layers are made up either of silver ions only or bromide ions only. Since the grains of photographic emulsions are precipitated from a medium containing a stoichiometric excess of halide ions to avoid inadvertent reduction of silver ions to silver atoms (and resultant photographic fog), in practice the surface tier of ions on silver bromide and bromiodide grains is always made up entirely of halide ions. The interim arrangement of a surface layer of silver ions is shown in Figure 4 to allow both the silver and bromide ion populations to be clearly viewed.

The five remaining achievable crystallographic forms for cubic crystal lattice silver halides are not favored.

(3) *The Rhombic Dodecahedral or {110} Form* In a few instances silver halide grains having faces of the rhombic dodecahedral form have been observed. A regular rhombic dodecahedral grain 7 is shown in Figure 5. The rhombic dodecahedral grain is bounded by twelve identical crystal faces. These crystal faces are referred to as rhombic dodecahedral or {110} (or, less commonly in reference to silver halide grains, {220}) crystal faces. Although the rhombic dodecahedral crystal shape can be visually identified in regular grains, in grains of more complex shapes the presence of rhombic dodecahedral crystal faces is not always visually verifiable.

Rhombic dodecahedral crystal faces can be theoretically hypothesized to consist of alternate rows of silver ions and halide ions. Figure 6 is a schematic illustration analogous to Figures 2 and 4, wherein it can be seen that the surface tier of ions is formed by repeating pairs of silver bromide ion parallel rows, indicated by lines 8a and 8b, respectively. In Figure 6 a portion of the next tier of ions lying below the surface tier is shown to illustrate their relationship to the surface tier of ions.

(4)-(7) There are four additional crystallographic forms which, though rare, can be exhibited by cubic crystal lattice structures:

(4) *The Tetrahexahedral or {hk0} Form*, where 0 is zero, h and k are integers >0 and $h \neq k$, is the subject matter of Maskasky U.S. Patent 4,680,255;

(5) *The Trisoctahedral or {hhl} Form*, where h and l are integers >0 and $h > l$, is the subject matter of Maskasky U.S. Patent 4,680,256;

(6) *The Hexoctahedral or {hkl} Form*, where h, k and l are integers >0 and $h > k > l$, is the subject matter of Maskasky U.S. Patent 4,680,254; and

(7) *The Icositetrahedral or {hll} Form*, where $h > l$, crystal forms are illustrated by Maskasky U.S. Patent 4,724,200.

Each of the {hk0}, {hhl}, {hkl} and {hll} crystal faces are similar to the {100} and {110} crystal faces and different from the {111} crystal faces in having both silver and halide ions at their surface, albeit in unique patterns in each instance.

In addition to regular grains of a polyhedral shape produced by being bounded entirely by crystal faces of the same crystallographic form, it is not uncommon to observe regular silver halide grains bounded by both cubic and octahedral crystal faces. Such grains are commonly referred to as cubo-octahedral grains. This is illustrated in Figure 7, wherein cubo-octahedral grains 9 and 10 are shown along with cubic grain 1 and octahedral grain 5. The cubo-octahedral grains have fourteen crystal faces, six cubic crystal faces and eight octahedral crystal faces, and for that reason they are sometimes alternatively referred to as tetradecehedral grains. Analogous combinations of cubic and/or octahedral crystal faces with the other known crystal faces are possible.

Further diversity in silver halide grain shape can be attributed to irregularities in the grains, such as twin planes or screw dislocations. Irregular grains of distinctive shapes, often observed in minor proportions, such as tabular silver bromide grains having {111} crystal faces, have been the subject of many silver halide crystallographic studies. Klein et al, "Formation of Twins of AgBr and AgCl Crystals in Photographic Emulsions", *Photographische Korrespondenz*, Vol. 99, No. 7, pp.99-102 (1963) describes a variety of singly and doubly twinned silver halide crystals having cubic and octahedral crystal faces. Klein et al is of interest in illustrating the variety of shapes which twinned silver halide grains can assume while still

exhibiting only cubic or octahedral crystal faces.

Although doubly twinned silver bromide and silver bromiodide grains bounded by octahedral or {111} crystal planes were long known to photographic scientists, as illustrated by Klein et al, it was not until the early 1980's that a variety of photographic advantages, most notably improved speed-granularity relationships, were realized to be attainable from silver bromide and bromiodide emulsions in which the majority of the total grain population based on grain projected area is accounted for by tabular grains satisfying the mean tabularity relationship:

$$D/t^2 > 25$$

where

D is the equivalent circular diameter (ECD) in micrometers of the tabular grains and

t is the thickness in micrometers of the tabular grains.

High ($D/t^2 > 25$) tabularity silver bromide and silver bromiodide emulsions are illustrated by Wilgus et al U.S. Patent 4,434,226 and Kofron et al U.S. Patent 4,439,520. The conditions necessary to achieve parallel twin plane formation in the grains and thereby achieve a tabular and preferably high tabularity grain configuration is taught to require a large stoichiometric excess of bromide ions and hence conditions that dictate the formation of {111} crystal faces on the grains.

Tani, "Quantitative Determination of Crystal Habit of Silver Halide Grains Through its Influence on Dye Adsorption", *Journal of Imaging Science*, Vol. 29, No. 5, Sept.-Oct. 1985, pp. 165-171, reports a technique for quantitatively determining the percentage of the total surface area of silver halide grains provided by {100} and {111} crystal faces. This is achieved by employing a dye that preferentially adsorbs to {100} crystal faces and which exhibits an absorption peak at a reference wavelength when adsorbed to {111} crystal faces that is otherwise absent. By adding small increments of the dye to an emulsion and monitoring increases in the reflection extinction of the emulsion at the reference wavelength, two transitions can be identified on plotting the data. First, a sharp rise in the reflection extinction occurs after a monomolecular layer of the dye has formed on all of the {100} crystal face area, so that subsequently added dye is directed to the {111} crystal faces. Finally, a point is reached at which a monomolecular layer of the dye occupies the entire available surface area of the grains, indicated by a second transition. Further dye addition beyond the second transition results in little further increase in reflection extinction. From the observations it is possible to calculate the percentage of the total grain surface area occupied by {111} and {100} crystal faces. Tani reports observation of regular cubic, octahedral, and tetradecahedral grains. No tabular grain emulsion is reported by Tani.

Maskasky U.S. Patent 4,643,966 reports tabular grain emulsions in which the major faces of the tabular grains are ruffled by pyramidal deposits of silver halide lying in non-{111} crystallographic planes. Because of the ruffling, the tabular grains do not have major faces lying in {111} crystallographic planes.

Hexacoordination complexes have been introduced into silver halide grains as dopants to modifying photographic properties. McDugle et al U.S. Patent 4,933,272 suggests doping with coordination complexes containing nitrosyl or thionitrosyl ligands and transition metals. Marchetti et al U.S. Patent 4,937,180 suggests doping silver bromide grains optionally containing iodide with a hexacoordination complex of rhenium, ruthenium or osmium with at least four cyanide ligands. McDugle et al U.S. Patent 4,981,781 discloses doping silver halide grains with hexacoordination complexes of a heavy transition metal chosen from groups 6, 7 and 8 of the periodic table of elements and at least one oxo ligand.

In one aspect, this invention is directed to a photographic emulsion comprised of a dispersing medium and silver bromide or silver bromiodide grains. At least 70 percent of the total projected area of the grains is accounted for by tabular grains having a thickness of less than $0.3 \mu\text{m}$ and a mean tabularity of greater than 25. The tabular grains have opposed parallel major faces and edge surfaces joining the parallel major faces of the tabular grains.

The emulsions are characterized in that the opposed parallel major faces of the tabular grains lie in {111} crystallographic planes and less than 75 percent of the edge surfaces of the tabular grains lie in {111} crystallographic planes.

The emulsions of the invention exhibit unexpectedly improved photographic properties. The emulsions exhibit improved speed-granularity relationships--that is, increased speed as compared to emulsions exhibiting similar granularity and reduced granularity as compared to emulsions exhibiting similar speed. The emulsions offer the capability of improved photoefficiency by reason of having a unique structure that works against recombination of photogenerated hole-electron pairs. When spectrally sensitized, the emulsions exhibit reduced dye desensitization and increased latent image stability on keeping.

Further, the novel grain structure required by the emulsions of the invention and the advantages which

are imparted are compatible with conventional high tabularity silver bromide and bromiodide emulsion structures and the advantages they are known to produce. Thus, the invention can be employed to enhance further the highest performance high tabularity silver bromide and bromiodide emulsions heretofore known in the art.

The invention directed to an improvement of silver bromide and bromiodide tabular grain emulsions. The emulsions of the invention are comprised of a dispersing medium and silver bromide or silver bromiodide grains. At least 70 percent of the total projected area of the grains forming the emulsion is accounted for by tabular grains having a thickness of less than $0.3\text{ }\mu\text{m}$ and a mean tabularity of greater than 25. The term "mean tabularity" is employed in its art recognized usage to indicate the relationship:

$$D/t^2$$

where

D is the equivalent circular diameter (ECD) in micrometers of the tabular grains and

t is the thickness in micrometers of the tabular grains.

The term "high tabularity" is employed to indicate a mean tabularity of greater than 25--i.e., $D/t^2 > 25$.

The tabular grains of the high tabularity silver bromide and bromiodide emulsions of the invention have opposed parallel major faces and edge surfaces joining the parallel major faces of the tabular grains. The opposed parallel major faces of the tabular grains lie in $\{111\}$ crystallographic planes and are thus similar to those of conventional high tabularity emulsions.

The invention is predicated upon selectively modifying the edge surfaces of the tabular grains so that less than 75 percent of the edge surfaces of the tabular grains lie in $\{111\}$ crystallographic planes.

Stated another way, the edges of the tabular grains exhibit a high ($> 25\%$) cubicity. High edge cubicity is realized when greater than 25 percent of total edge surface area of the tabular grain emulsion lies in crystallographic planes other than $\{111\}$ crystallographic planes--i.e., non- $\{111\}$ crystallographic planes. Since in the overwhelming majority of instances only octahedral $\{111\}$ and cubic $\{100\}$ crystallographic planes are present in silver halide emulsions, the non- $\{111\}$ crystallographic planes are in most instances $\{100\}$ crystallographic planes. However, all non- $\{111\}$ crystallographic planes share the significant common feature of presenting both silver and halide ions at their surface, whereas only $\{111\}$ crystallographic planes present only a halide ion surface. Thus, "cubicity", herein employed to indicate a mixed positive and negative ion crystallographic surface characteristic, distinguishes all non- $\{111\}$ crystal faces from $\{111\}$ crystal faces.

While the advantages of increasing the edge cubicity of the tabular grains has been demonstrated in the Examples below and thus has been proven independent of any theory, there are, in fact, excellent theoretical bases for concluding that an edge increase in the cubicity of tabular grains can enhance their imaging efficiency and sensitivity. When a photon is absorbed within a silver bromide or bromiodide grain, a hole-electron pair is generated. That is, an electron is lifted out of its valence band orbital into the conduction band. Forming a developable latent image depends on conduction band electrons generated by photon capture reducing silver ions to produce in close spatial proximity two or three atoms of silver. In the majority of instances latent images are formed at the surface of a grain, since the physical imperfections at the surfaces of the grains offer the best opportunity for vicinal reduction of silver ions to silver atoms.

When an octahedral grain is modified by incorporation of two or more parallel twin planes, it assumes a tabular shape, but remains bounded by $\{111\}$ crystal faces. The $\{111\}$ crystal faces are formed by a surface layer of halide ions and thus present a net negative surface charge. Since the grain surface has a net negative charge, migration of conduction band electrons toward the grain surface is inhibited and this in turn works against surface latent image formation. Further, since all of the surfaces of the grain are essentially similar in terms of presenting a similar net negative charge, the grain surface does not itself function to gather conduction band electrons into a vicinal area as required for latent image formation.

By forming the tabular grains with parallel major faces lying in $\{111\}$ crystallographic planes and edge surfaces lying to an increased extent in non- $\{111\}$ crystallographic planes, the grains are formed so that their major faces exhibit a net negative charge while their edge surfaces by reason of their higher cubicity exhibit a balance of positive and negative ions that is positively shifted as compared to the major faces. Thus, conduction band electrons experience at least some charge repulsion from the major surfaces of the tabular grains (as in conventional tabular grain emulsions) and a relative charge attraction to the edge surfaces of the tabular grains. The latter increases the efficiency of latent image formation in three different ways. First, migration of the conduction band electron to a grain surface, where latent image formation is more likely to occur, is facilitated. Second, the edge surfaces of the tabular grains account for only a small fraction of the total tabular grain surface area. Thus, by attracting conduction band electrons selectively to

edge grain faces the probability of vicinal location of the requisite number of silver atoms for latent image formation is increased. Third, the photo-generated hole, representing a positive charge site, is attracted to the {111} major faces of the tabular grains while the photo-generated electrons are being attracted to grain edges. This functions to separate spatially each photo-generated hole-electron pair, thereby reducing the possibility of mutual annihilation by recombination.

The net result is to increase the latent image forming efficiency and hence the speed of the high edge cubicity tabular grain silver bromide and bromiodide emulsions of the invention. In theory the tabular grain emulsions of the invention can benefit from edge cubicities ranging up to 100%. That is, theoretically, performance enhancement should be realized by increasing the proportion of the edge surfaces lying in non-{111} crystal planes until they account for all or substantially of the total edge surface area of the tabular grains. However, since tabular grains inherently favor {111} crystal faces, in practice when the most convenient edge modification techniques are employed, the edge cubicities of the tabular grains are typically in the range of >25% to about 50% of total edge surface area of the tabular grains.

Although the first reported high tabularity emulsions exhibited significant populations of nontabular grains, subsequent optimizations of precipitation procedures have produced emulsions in which much higher proportions of tabular grains are present. In the emulsions of the present invention tabular grains account for at least 70 percent of the total grain projected area. Emulsions in which the tabular grains account for at least 90 percent of the total grain population are preferred, and, optimally, the tabular grains account for all or nearly all of the total grain projected area.

The technique employed for measuring edge cubicities of tabular grain emulsions is that reported by Tani, cited above, which was developed for nontabular emulsions. The technique of Tani observes total grain cubicity. When the grain population consists essentially of tabular grains, total grain cubicity corresponds to edge cubicity, since the major faces of the tabular grains are known to lie in {111} crystallographic planes. When coprecipitated nontabular grains (including thick singly twinned grains) are also present, these grains are also known to exhibit {111} crystallographic forms. Again, the total measured cubicity can be attributed to the edges of the tabular grains. It is contemplated that the edge cubicity of the tabular grains will be determined following precipitation of the emulsions and before blending with separately prepared emulsions. However, when two or more emulsions of significantly differing crystal habit are blended prior to determining cubicity, usually a combination of microscopic and statistical analyses can be relied upon to determine at least a minimum possible edge cubicity of a coprecipitated tabular grain population.

It is generally preferred that the tabular grains contain at least a minor amount of iodide to increase photographic sensitivity. It is recognized in the art that iodide concentrations of as little as 0.1 mole percent, based on silver, are effective to increase photographic speed. Usually iodide concentrations in the range of from about 1 to 20 mole percent are contemplated, although high iodide concentrations, ranging up to the saturation limit of iodide in silver bromide are contemplated.

From the relationship D/t^2 , discussed above, it is apparent that the tabularities of the emulsions (and hence the performance benefits attributable to the tabular grain shape) increase progressively as the mean thicknesses of the tabular grains are reduced. It is therefore preferred that the tabular grains of the emulsions have a mean thickness of less than 0.2 μm . It is generally preferred that the emulsions exhibit tabularities of greater than 40 and optimally greater than 100. Tabularities of up to 400 are readily realized, with tabularities of up to 1000 or more being attainable. The average aspect ratios of the tabular grains of the emulsions are preferably greater than 8:1, usually greater than 12:1, and optimally greater than 20:1. Average aspect ratios can range up to range up to 200:1 or more, but typically range up to about 100:1.

Once a high tabularity silver bromide or bromiodide emulsion has been produced exhibiting a high edge cubicity the emulsion can be employed to advantage, with or without intentional chemical sensitization, to record imagewise exposures to which it possesses native sensitivity--that is, to wavelengths of less than about 450 nm. By conventional spectral sensitization the imaging utility of the emulsions can be extended throughout the visible as well as into the near infrared portions of the spectrum. Conventional chemical and spectral sensitizations summarized by Research Disclosure, Vol. 308, December 1989, Item 308,119, Sections III and IV, compatible with negative-working, surface latent image emulsions are contemplated. Research Disclosure is published by Kenneth Mason Publications, Ltd., Dudley Annex, 21a North Street, Emsworth, Hampshire PO10 7DQ, England. Preferred procedures for chemically and spectrally sensitizing silver bromide and silver bromiodide tabular grain emulsions are disclosed by Kofron et al U.S. Patent 4,439,520 and Maskasky U.S. Patent 4,435,501.

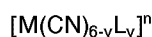
An important advantage offered by the high edge cubicity tabular grain emulsions of the invention is that different portions of the grain surface can be used for chemical and spectral sensitization. This provides performance advantages that cannot be realized when one or both of chemical and spectral sensitizations

are applied indiscriminately to all available grain surfaces. As progressively larger amounts of dye are adsorbed to the surface of silver halide grains, the sensitivity of the emulsions to exposures within the spectral region of absorption by the dye is enhanced. However, in many instances further increases of dye concentrations beyond that which produces a maximum sensitivity results in a pronounced reduction in the sensitivity of the emulsion, referred to as dye desensitization. By constructing the tabular grains with high levels of edge cubicity it is possible to form the latent image sites at the non-{111} crystal surfaces. By employing a spectral sensitizing dye that is selective to the {111} major faces of the tabular grains the sites of spectral and chemical sensitization can be separated. This allows higher levels of dye to be adsorbed to the tabular grain major faces, which are relied upon for photon capture during exposure, without desensitizing the emulsion. Spectral sensitizing dye concentrations up to the full amount required to produce a monomolecular coverage of all {111} crystal surfaces are contemplated. The high edge cubicity tabular grains of the invention are particularly advantageous when spectrally sensitized prior to chemical (including epitaxial) sensitization, as taught by Kofron et al U.S. Patent 4,439,520 and Maskasky U.S. Patent 4,435,501, both cited above.

Apart from the features specifically described above, the tabular grain emulsions of the invention and the elements in which they are incorporated can take any convenient conventional form. Research Disclosure, Item 308,119, cited above, provides a summary of these conventional features. The tabular grains of the emulsion can contain any of a variety of conventional features known to be compatible with negative-working, surface latent image forming grain structures, such as those summarized in Section I. In addition to the grains described the emulsions include a dispersing medium or vehicle comprised of a peptizer for the grains as formed, additional peptizer added after precipitation to act as a binder for coating, and, optionally, latex and other binder components to improve photographic properties and improve coating characteristics. Preferred peptizers are hydrophilic colloids, such as gelatin and gelatin derivatives (i.e., gelatino-peptizers). Conventional vehicles are summarized in Section IX. The emulsions can be washed as described in Section II. The emulsions can contain antifoggants and stabilizers, as described in Section VI. The emulsions can be particularly adapted for use in color materials, as described in Section VII. The vehicles can include hardeners, as set forth in Section X. Additional features for element fabrication and processing are set forth in Sections XI to XXIII.

It has been observed quite unexpectedly that when the high tabularity, high cubicity emulsions of this invention contain a hexacoordination complex dopant containing a metal from group 8 of the periodic table of elements and at least 3 cyano (CN) ligands an unexpected increase in the sensitivity of the emulsion is realized. All references the periodic table of elements refer to the form adopted by the American Chemical Society as published in the *Chemical and Engineering News*, Feb. 4, 1985, p. 26. Thus, the transition metal elements contemplated are iron, ruthenium and osmium, with iron being particularly preferred.

In a specifically contemplated form the hexacoordination complex dopants satisfy the formula:



where

- L is a bridging ligand,
- M is Fe, Ru or Os,
- y is the integer zero, 1, 2 or 3 and
- n is -3 or -4.

Since the bridging ligand L can itself in one or more occurrence be a cyano (CN) ligand, it is apparent that the coordination complex can contain 3, 4, 5 or 6 cyano (CN) ligands.

When one or more of the bridging ligands L are not cyano (CN) ligands, they can take any convenient conventional form. A variety of conventional bridging ligands are disclosed in McDugle et al U.S. Patents 4,933,272 and 4,981,781, Marchetti et al U.S. Patent 4,937,180 and Keevert et al U.S. Patent 4,945,035. Preferred bridging ligands other than cyano (CN) ligands are monoatomic monodentate ligands, such as halides. Fluoride, chloride, bromide and iodide ligands are all specifically contemplated. Multielement ligands, such as azide and thiocyanate ligands are also specifically contemplated.

The following are specific hexacoordination complexes contemplated for use as dopants in the high tabularity, high cubicity emulsions of the invention:

- TMC-1 $[Fe(CN)_6]^{4-}$
- TMC-2 $[Ru(CN)_6]^{4-}$
- TMC-3 $[Os(CN)_6]^{4-}$
- TMC-4 $[FeF(CN)_5]^{4-}$
- TMC-5 $[RuF(CN)_5]^{4-}$

	TMC-6	$[\text{OsF}(\text{CN})_5]^{-4}$
	TMC-7	$[\text{FeCl}(\text{CN})_5]^{-4}$
	TMC-8	$[\text{RuCl}(\text{CN})_5]^{-4}$
	TMC-9	$[\text{OsCl}(\text{CN})_5]^{-4}$
5	TMC-10	$[\text{FeBr}(\text{CN})_5]^{-4}$
	TMC-11	$[\text{RuBr}(\text{CN})_5]^{-4}$
	TMC-12	$[\text{OsBr}(\text{CN})_5]^{-4}$
	TMC-13	$[\text{FeI}(\text{CN})_5]^{-4}$
	TMC-14	$[\text{RuI}(\text{CN})_5]^{-4}$
10	TMC-15	$[\text{OsI}(\text{CN})_5]^{-4}$
	TMC-16	$[\text{FeF}_2(\text{CN})_4]^{-4}$
	TMC-17	$[\text{RuF}_2(\text{CN})_4]^{-4}$
	TMC-18	$[\text{OsF}_2(\text{CN})_4]^{-4}$
	TMC-19	$[\text{FeCl}_2(\text{CN})_4]^{-4}$
15	TMC-20	$[\text{RuCl}_2(\text{CN})_4]^{-4}$
	TMC-21	$[\text{OsCl}_2(\text{CN})_4]^{-4}$
	TMC-22	$[\text{FeBr}_2(\text{CN})_4]^{-4}$
	TMC-23	$[\text{RuBr}_2(\text{CN})_4]^{-4}$
	TMC-24	$[\text{OsBr}_2(\text{CN})_4]^{-4}$
20	TMC-25	$[\text{FeF}_3(\text{CN})_3]^{-4}$
	TMC-26	$[\text{RuF}_3(\text{CN})_3]^{-4}$
	TMC-27	$[\text{OsF}_3(\text{CN})_3]^{-4}$
	TMC-28	$[\text{FeCl}_3(\text{CN})_3]^{-4}$
	TMC-29	$[\text{RuCl}_3(\text{CN})_3]^{-4}$
25	TMC-30	$[\text{OsCl}_3(\text{CN})_3]^{-4}$
	TMC-31	$[\text{OsBr}_3(\text{CN})_3]^{-4}$
	TMC-32	$[\text{FeBr}_3(\text{CN})_3]^{-4}$
	TMC-33	$[\text{RuBr}_3(\text{CN})_3]^{-4}$
	TMC-34	$[\text{Fe}(\text{CN})_5(\text{OCN})]^{-4}$
30	TMC-35	$[\text{Ru}(\text{CN})_5(\text{OCN})]^{-4}$
	TMC-36	$[\text{Os}(\text{CN})_5(\text{OCN})]^{-4}$
	TMC-37	$[\text{Fe}(\text{CN})_5(\text{SCN})]^{-4}$
	TMC-38	$[\text{Ru}(\text{CN})_5(\text{SCN})]^{-4}$
	TMC-39	$[\text{Os}(\text{CN})_5(\text{SCN})]^{-4}$
35	TMC-40	$[\text{Fe}(\text{CN})_5(\text{HOH})]^{-3}$
	TMC-41	$[\text{Ru}(\text{CN})_5(\text{HOH})]^{-3}$
	TMC-42	$[\text{Os}(\text{CN})_5(\text{HOH})]^{-3}$

Improvements in sensitivity can be realized when the dopants are incorporated in concentrations ranging from 1 to 150 molar parts per million (mppm), based on silver. Preferred average concentrations are in the range of from 30 to 100 mppm. It is possible to concentrate the dopant within a limited region of the grain (e.g., within a core or subshell) as it is being grown, as demonstrated in the Examples below. Even though portions of the grains contain little or no dopant and other portions contain relatively high concentrations of the dopant increased imaging efficiencies can still be realized so long as the grains maintain overall average dopant concentrations within the ranges noted above. It has been observed that optimum results are observed when the maximum concentration of dopant at any location within the grain remains within the average concentration ranges set out above.

Examples

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

Comparative Example 1 (AgBr, Example 9, Saitou et al U.S. Patent 4,797,354)

In a 4-liter reaction vessel was placed an aqueous gelatin solution (composed of 1 liter of water, 7 g of deionized alkali-processed gelatin, 4.5 g of potassium bromide, 1.2 ml of 1 N potassium hydroxide solution and having pBr of 1.42) and while keeping the temperature thereof at 30 °C., 25 ml of an aqueous solution of silver nitrate (containing 8.0 g of silver nitrate) and 25 ml of an aqueous solution of potassium bromide (containing 5.8 g of potassium bromide) were simultaneously added thereto over a period of 1 minute at a

rate of 25 ml/min. Then, an aqueous gelatin solution (composed of 1950 ml of water, 90 g of deionized alkali-processed gelatin, 15.3 ml of 1 N aqueous potassium hydroxide solution, and 3.6 g of potassium bromide) was added to the reaction vessel and the temperature of the mixture was raised to 75 °C over a period of 10 minutes. Thereafter, ripening was performed for 50 minutes.

The mixture was then transferred to a 12-liter vessel, into which 200 ml of an aqueous silver nitrate solution (containing 90 g of silver nitrate) was added at a rate of 20 ml/min. Twenty-five seconds after commencing the addition of silver nitrate, 191.6 ml of an aqueous potassium bromide solution (containing 61.2 g of potassium bromide) was added to the mixture at a rate of 20 ml/min., the additions of both solutions being finished at the same time. Thereafter, the resultant mixture was stirred for 2 minutes, and then 2,000 ml of an aqueous silver nitrate solution (containing 900 g of silver nitrate) and 2,000 ml of a potassium bromide solution (containing 636.9 g of potassium bromide) were simultaneously added to the aforesaid mixture at a rate of 40 ml/min for the first 20 minutes and 60 ml/min for the subsequent 20 minutes. Then, after stirring the mixture for 1 minute, the silver halide emulsion thus obtained was washed and redispersed. The emulsion grains consisted essentially of silver bromide.

The properties of grains of this emulsion were as follows:

Average Grain ECD: 1.20 μm

Average Grain Thickness: 0.162 μm

Average Aspect Ratio: 7.4

Average Tabularity: 45.7

Coefficient of Variation based on Total Grains: 21.3%

Example 2 (AgBr)

In a 4-liter reaction vessel was placed an aqueous gelatin solution (composed of 1 liter of water, 2.5 g of oxidized alkali-processed gelatin, 4.0 ml of 4 N nitric acid solution, 1.12 g of sodium bromide and having pAg of 9.39) and 1.57 wt%, based on total silver introduced up to the beginning of post-ripening grain growth stage, of PLURONIC™-31R1 (a polyalkylene oxide block copolymer surfactant having two terminal lipophilic block units each consisting of twenty-five 1,2-propylene oxide repeating units, the terminal block units being joined by a central hydrophilic block unit consisting of seven ethylene oxide repeating units) and, while keeping the temperature thereof at 45 °C., 8.3 ml of an aqueous solution of silver nitrate (containing 2.26 g of silver nitrate) and equal volume of an aqueous solution of sodium bromide (containing 1.44 g of sodium bromide) were simultaneously added thereto over a period of 1 minute at a constant rate. Then, into the mixture was added 14.2 ml of an aqueous sodium bromide solution (containing 1.46 g of sodium bromide) after 1 minute of mixing. Temperature of the mixture was raised to 60 °C over a period of 9 minutes. At that time, 65 ml of an aqueous ammoniacal solution (containing 6.7 g of ammonium sulfate and 48 ml of 2.5 N sodium hydroxide solution) was added into the vessel and mixing was conducted for a period of 9 minutes. Then, 105.5 ml of an aqueous gelatin solution (containing 16.7 g of oxidized alkali-processed gelatin and 22 ml of 4 N nitric acid solution) was added to the mixture over a period of 2 minutes. Thereafter, 25 ml of an aqueous silver nitrate solution (containing 6.8 g of silver nitrate) and equal volume of an aqueous sodium bromide solution (containing 4.4 g of sodium bromide) were added at a constant rate for a period of 10 minutes. Then, 225 ml of an aqueous silver nitrate solution (containing 61.1 g of silver nitrate) and equal volume of an aqueous sodium bromide solution (containing 38.9 g of sodium bromide) were simultaneously added to the aforesaid mixture at constant ramp starting from respective rate of 2.5 ml/min and 2.6 ml/min for the subsequent 30 minutes. Subsequently, 469 ml of an aqueous silver nitrate solution (containing 127.4 g of silver nitrate) and 466 ml of an aqueous sodium bromide solution (containing 80.5 g of sodium bromide) were simultaneously added to the aforesaid mixture at constant rate over a period of 37.5 minutes. The silver halide emulsion thus obtained was washed and redispersed.

The properties of grains of this emulsion were as follows:

Average Grain ECD: 1.26 μm

Average Grain Thickness: 0.144 μm

Average Aspect Ratio of the Grains: 8.8

Average Tabularity of the Grains: 60.8

Coefficient of Variation based on Total Grains: 6.3%

Comparative Example 3 ($\text{AgBr}_{0.99}\text{I}_{0.01}$)

Example 1 was repeated, except that 159 microgram of ammonium hexachlororhodate (III) was introduced over a period of 2.5 min after emulsion was transferred to the 12-liter vessel, and that 1 mole

percent of potassium iodide was additionally added to the potassium bromide solution for the subsequent precipitation. The emulsion thus made contained 1 mole% of iodide and 7.23×10^{-8} gram atom of ammonium hexachlororhodate (III) per silver mole.

The properties of grains of this emulsion were as follows:

- 5 Average Grain ECD: $1.30 \mu\text{m}$
- Average Grain Thickness: $0.148 \mu\text{m}$
- Average Aspect Ratio of the Grains: 8.8
- Average Tabularity of the Grains: 59.3
- Coefficient of Variation based on Total Grains: 19.2%

10

Example 4 ($\text{AgBr}_{0.99}\text{I}_{0.01}$)

- In a 4-liter reaction vessel was placed an aqueous gelatin solution (composed of 1 liter of water, 1 g of alkali-processed gelatin, 1 ml of 4 N nitric acid solution, 2.44 g of sodium bromide and having pAg of 9.71, and 5.21 wt%, based on total silver introduced up to the beginning of post-ripening grain growth stage, of PLURONIC™-L63 (a polyalkylene oxide block copolymer surfactant having two terminal hydrophilic block units each consisting of nine ethylene oxide repeating units, the terminal block units being joined by a central lipophilic block unit consisting of thirty-two 1,2-propylene oxide repeating units) and, while keeping the temperature thereof at 45°C ., 6.7 ml of an aqueous solution of silver nitrate (containing 0.91 g of silver nitrate) and equal volume of an aqueous solution of sodium bromide (containing 0.63 g of sodium bromide) were simultaneously added thereto over a period of 1 minute at a constant rate. After 1 minute of mixing, temperature of the mixture was raised to 60°C over a period of 9 minutes. At that time, 28.5 ml of an aqueous ammoniacal solution (containing 1.68 g of ammonium sulfate and 11.8 ml of 2.5 N sodium hydroxide solution) was added into the vessel and mixing was conducted for a period of 9 minutes.
- Thereafter, 88.7 ml of an aqueous gelatin solution (containing 16.7 g of alkali-processed gelatin and 5.3 ml of 4 N nitric acid solution) was added to the mixture over a period of 2 minutes. 31.6 microgram of ammonium hexachlororhodate (III) was subsequently introduced over a period of 2.5 min. After then, 7.5 ml of an aqueous silver nitrate solution (containing 1.0 g of silver nitrate) and 7.3 ml of an aqueous sodium bromide solution (containing 0.68 g of sodium bromide) were added at a constant rate for a period of 5 minutes. Then, 474.7 ml of an aqueous silver nitrate solution (containing 129 g of silver nitrate) and 473.6 ml of an aqueous halide solution (containing 81 g of sodium bromide and 1.3 g of potassium iodide) were simultaneously added to the aforesaid mixture at constant ramp starting from respective rate of 1.5 ml/min and 1.6 ml/min for the subsequent 64 minutes. Then, 253.3 ml of an aqueous silver nitrate solution (containing 68.9 g of silver nitrate) and 251.1 ml of an aqueous halide solution (containing 43 g of sodium bromide and 0.7 g of potassium iodide) were simultaneously added to the aforesaid mixture at constant rate over a period of 19 minutes. The silver halide emulsion thus obtained contained 1 mole% of iodide and 7.23×10^{-8} gram atom of ammonium hexachlororhodate (III) per silver mole.

The properties of grains of this emulsion were as follows:

- 40 Average Grain ECD: $1.35 \mu\text{m}$
- Average Grain Thickness: $0.153 \mu\text{m}$
- Average Aspect Ratio of the Grains: 8.8
- Average Tabularity of the Grains: 57.7
- Coefficient of Variation based on Total Grains: 7.0%

45 Determination of Cubicity

- The cubicity of the tabular grain emulsions of Examples 1 to 4 inclusive was determined by a procedure similar to that of Tani, cited above. A continuous flow-cell reflection spectrometer was used to measure reflection extinction attributable to dye adsorption. Zwitterionic 3-ethyl-9-methyl-3'-(3-sulfobutyl) thiacyanobocyanine, hereinafter referred to as Dye A, was chosen for cubicity measurements. A 0.34 millimolar solution of Dye A was prepared in methanol. A sample of 10 grams of each emulsion was dispersed in a mixture of 93 ml of deionized water and 7 ml of methanol. The temperature of the emulsion sample and the flow-cell was then adjusted and maintained at 55°C . The dye solution was then added in increments of 0.5 ml at the rate of 0.1 ml/min. The interval between successive additions was 15 minutes. The reflectivity of the sample was monitored 14 minutes following dye addition by measuring extinction at 625 nm. By plotting dye addition versus extinction in optical density units a point on the curve was identified beyond which extinction rose sharply with further dye addition. This provided an indication of the total amount of dye required to provide saturation coverage of all non-{111} surfaces of the grains. A point on the plot of dye

addition versus extinction in optical density units was identified, at which the sharp rise of extinction, with further dye addition ceased, indicating dye coverage of all grains surfaces.

From microscopic examination of the grains of each emulsion sample it was possible to determine the mean equivalent circular diameter (ECD) and thickness (t) of the tabular grains. From this information the total surface area of each sample was calculated.

With this information the percent total cubicity (% ΣC) was calculated as follows:

$$\% \Sigma C = \frac{W \times \text{Avog. \#} \times \text{MAD} \times 100}{\text{MWD} \times \text{TSAS}}$$

where

W is the weight of Dye A required for the saturation coverage of all non-{111} surfaces;

Avog.# is Avagadro's Number;

MAD is the area that a molecule of the dye occupies;

MWD is the molecular weight of the dye; and

TSAS is the total grain surface area of the sample.

Percent total cubicity was then converted to percent edge cubicity (% EC) as follows:

$$\% EC = \% \Sigma C \times (ECD + 2t)/2t,$$

where ECD and t are as previously defined.

Sensitizations

Samples of each of Emulsions 1 to 4 inclusive were sensitized as follows:

Each emulsion sample was optimally sensitized with 70 mg/mole of sodium thiocyanate, 2.4 mg/mole of potassium tetrachloroaurate, 3.2 mg/mole of sodium thiosulfate pentahydrate, 60 mg/mole of Dye B, 3-ethyl-5-[N-(4-sulfobutyl)-4-(1H)pyridylidene], pyridinium salt, heat treated at 65°C for 35 min. To the finished emulsion were added 300 mg/mole of 5-methyl-s-triazole-(2-3-a)-pyrimidine-7-ol.

Coatings and Processing

The sensitized samples of the emulsions were compared as follows:

The emulsion of Comparative Example 1 was compared with the emulsion of Example 2 to provide a silver bromide comparison. The emulsion of Comparative Example 2 was compared with the emulsion of Example 4 to provide a silver bromiodide comparison. The emulsion comparisons were based on identical silver coverages, corresponding to silver coverages of 21.52 mg/GM² (200 mg/ft²) on transparent film support. The coatings were each processed in Developer A described in Table I for 1 min at 35°C and in Fixer A described in Table II for 30 sec.

Table I

Composition of Developer A	
	gram
Water	539.0
Potassium hydroxide, 45.5% solution	178.0
Sodium metabisulfite	145.0
Sodium bromide	12.0
2-butene-dioic acid (z), homopolymer, 50 % solution	13.0
Pentetic acid, pentasodium salt, 40% solution	15.0
Sodium hydroxide, 50% solution	56.0
Benzotriazole	0.4
1-Phenyl-5-mercaptopotetrazole	0.05
Boric acid	6.94
Diethylene glycol	110.0
Hydroquinone	75.0
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	2.9
Potassium carbonate, 47% solution	120.0

Table II

Composition of Fixer A	
	gram/liter
Ammonia thiosulfate	155.0
Sodium metabisulfite	190.0
Sodium acetate/acetic acid	25.0
Sodium borate, 5-hydrate	11.8
Aluminum sulfate	6.6

The photographic responses for the coatings with 1/10 sec exposure to 3000° K light temperature are summarized in Tables III and IV. The superior photographic performance demonstrated by the invention emulsions, Emulsions 2 and 4, correlates increased cubicity (non-{111} grain surfaces) with increased speed with matching fog. Speed in Tables III and IV is measured at a density of 1.0 above fog. Emulsions 2 and 4 also demonstrated increased contrast as compared to Comparative Emulsions 1 and 3, but this was unrelated to differences in cubicity.

Table III

Emulsion	Fog	Speed	% ΣC	% EC
1 (Comparison)	0.04	153	3.3	15.2
2 (Invention)	0.04	213	6.3	33.9

Comparative Emulsion 3 and Emulsion 4 are similarly compared in Table IV. Again, the correlation between increased speed and increased cubicity is apparent.

Table IV

Emulsion	Fog	Speed	% ΣC	% EC
3 (Comparison)	0.06	221	3.8	20.5
4 (Invention)	0.05	233	7.5	40.5

The comparison of Emulsions 3 and 4 were repeated as described above, except that the exposure times were reduced to 10^{-5} seconds to demonstrate performance under high intensity conditions of exposure. The results are summarized in Table V.

Table V

Emulsion	Fog	Speed	% ΣC	% EC
3 (Comparison)	0.03	145	3.8	20.5
4 (Invention)	0.03	160	7.5	40.5

Examples 5 to 12 inclusive

These examples have as their purpose to demonstrate the advantageous properties of high tabularity, high cubicity emulsions according to this invention when doped with hexacoordination complexes containing a group 8 metal and at least 3 cyano (CN) ligands.

Example 5

Emulsion 5A

Nine solutions were prepared as follows:

Solution 1 (1)	
Pluronic™ -31R1	0.6 gm
Oxidized gelatin (bone)	4.8 gm
Distilled water	5948 ml

Solution 2 (1)	
Silver Nitrate	22.7 gm
Distilled water	163 ml

Solution 3 (1)	
Sodium Bromide	14.5 gm
Distilled water	164 ml

EP 0 515 894 A1

Solution 4 (1)	
Pluronic™ -31R1	1.0 gm
Sodium Bromide	13.4 gm
Distilled water	127 ml

Solution 5 (1)	
Oxidized gelatin (bone)	100 gm
Distilled water	918 ml

Solution 7 (1)	
Sodium Bromide	798 gm
Distilled water	4414 ml

Solution 8 (1)	
Phthalated gelatin (bone)	255 gm
Distilled water	1600 ml

Solution 9 (1)	
Gelatin (bone)	123 gm
Distilled water	1660 ml

Solution 1 (1) was adjusted to a pH of 1.8 with nitric acid at 45° C. The pAg of solution 1 (1) was adjusted to pAg of 9.36 with sodium bromide. Solutions 2 (1) and 3 (1) were simultaneously run into solution 1 (1) at a constant rate for one minute and held for an additional minute when solution 4 (1) was added. The temperature of this mixture was adjusted to 60° C after which the mixture was treated with ammonium sulfate and sodium hydroxide to pH of 9.5 for 2 minutes. Solution 5 (1) was then added and the mixture was held for one minute. The pH was then adjusted to 5.8 with nitric acid. Simultaneous introduction of solutions 2 (1) and 3 (1) was resumed at a constant rate for 5 minutes while controlling pAg at 9.36. Solutions 6 (1) and 7 (1) were then introduced at an accelerated rate for 64 minutes and continued for 19 minutes at a constant rate. The pAg was controlled at 9.36 while solutions 6 (1) and 7 (1) were added. The temperature was then adjusted to 40° C and solution 8 (1) was added. After 5 minutes, the pH was adjusted to 3.5, the temperature reduced to 20° C and the mixture allowed to settle. When settling was complete, the liquid layer was decanted. The depleted volume was replaced with distilled water. The mixture was redispersed while the temperature was adjusted to 40° C and the pH adjusted to 5.5. The pH was adjusted to 3.5 and settling and decanting steps repeated. Solution 9 (1) was added, and the pH and pAg were adjusted to 5.5 and 8.2 respectively.

Emulsion 5B

A second emulsion (5B) was prepared like 5A with $K_4Fe(CN)_6$ at a formal concentration of 50 molar parts per million added in the salts from 1 to 90 percent of silver reagent addition, for an overall average concentration of 45 mppm based on silver.

Emulsion 5C

A third emulsion (5C) was prepared like 5A with $K_4Fe(CN)_6$ at a formal concentration of 50 molar parts per million added in the salts from 1 to 70 percent of silver reagent addition, for an overall average

EP 0 515 894 A1

concentration of 35 mppm based on silver.

Emulsion 5D

- 5 A fourth emulsion (5D) was prepared like 5A with $K_4Fe(CN)_6$ at a formal concentration of 250 molar parts per million added in the salts from 1 to 70 percent of silver reagent addition, for an overall average concentration of 175 mppm based on silver.

Emulsion 5E

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A fifth emulsion (5E) was prepared like 5A with $K_4Fe(CN)_6$ at a formal concentration of 250 molar parts per million added in the salts from 56 to 70 percent of silver reagent addition, for an overall average concentration of 35 mppm based on silver.

15 Emulsion 5F

A sixth emulsion (5F) was prepared like 5A with $K_4Fe(CN)_6$ at a formal concentration of 50 molar parts per million added in the salts from 56 to 70 percent of silver reagent addition, for an overall average concentration of 7 mppm based on silver.

20

Table VI

25	Emulsion Characteristics				
	Emulsion	equivalent circular diameter (ECD) (μm)	coefficient of ECD variation	thickness (μm)	grain volume (μm^3)
30	5A	1.06	8.3	0.13	0.11
	5B	1.02	9.5	0.11	0.09
	5C	1.20	9.3	0.11	0.11
	5D	1.20	9.2	0.11	0.11
	5E	1.22	8.2	0.11	0.12
	5F	1.20	9.6	0.10	0.12

35

Example 6

Emulsion 6A

- 40 Nine solutions were prepared as follows:

45

Solution 1 (2)	
Pluronic™ -31R1	4.0 gm
Distilled water	5948 ml

50

Solution 2 (2)	
Silver Nitrate	22.7 gm
Distilled water	163 ml

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EP 0 515 894 A1

Solution 3 (2)	
Sodium Bromide	14.5 gm
Distilled water	164 ml

5

Solution 4 (2)	
Sodium Bromide	13.4 gm
Distilled water	127 ml

10

Solution 5 (2)	
Pluronic™ -31R1	1.0 gm
Distilled water	918 ml

15

Solution 6 (2)	
Silver Nitrate	1261 gm
Distilled water	4402 ml

20

25

Solution 7 (2)	
Sodium Bromide	798 gm
Distilled water	4414 ml

30

Solution 8 (2)	
Phthalated gelatin (bone)	255 gm
Distilled water	1600 ml

35

Solution 9 (2)	
Gelatin (bone)	123 gm
Distilled water	1660 ml

40

45

50

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Solution 1 (2) was adjusted to a pH of 1.8 with nitric acid at 45°C. The pAg of solution 1 (2) was adjusted to pAg of 9.11 with sodium bromide. Solutions 2 (2) and 3 (2) were simultaneously run into solution 1 (2) at a constant rate for one minute and held for an additional minute when solution 4 (2) was added. The temperature of this mixture was adjusted to 60°C after which the mixture was treated with ammonium sulfate and sodium hydroxide to pH of 9.5 for 2 minutes. Solution 5 (2) was then added and the mixture was held for one minute. The pH was then adjusted to 5.8 with nitric acid. Simultaneous introduction of solutions 2 (2) and 3 (2) was resumed at a constant rate for 5 minutes while controlling pAg at 9.36. Solutions 6 (2) and 7 (2) were then introduced at an accelerated rate for 64 minutes and continued for 19 minutes at a constant rate. The pAg was controlled at 9.36 while solutions 6 (2) and 7 (2) were added. The temperature was then adjusted to 40°C and solution 8 (2) was added. After 5 minutes, the pH was adjusted to 3.5, the temperature reduced to 20°C and the mixture allowed to settle. When settling was complete, the liquid layer was decanted. The depleted volume was replaced with distilled water. The mixture was redispersed while the temperature was adjusted to 40°C and the pH adjusted to 5.5. The pH was adjusted to 3.5 and settling and decanting steps repeated. Solution 9 (2) was added, and the pH and pAg were adjusted to 5.5

and 8.2 respectively.

Emulsion 6B

- 5 A second emulsion (6B) was prepared like 6A with $K_4Fe(CN)_6$ at a formal concentration of 50 molar parts per million added in the salts from 1 to 70 percent of silver reagent addition, for an overall average concentration of 35 mppm based on silver.

Table VII

10

Emulsion Characteristics				
Emulsion	equivalent circular diameter (ECD) (μm)	coefficient of ECD variation	thickness (μm)	grain volume (μm^3)
6A	2.03	9.9	0.15	0.46
6B	1.98	7.4	0.15	0.45

15

20 Example 7

Emulsion 7A

Nine solutions were prepared as follows:

25

Solution 1 (3)	
Pluronic™ -31R1	1.2 gm
Distilled water	5948 ml

30

Solution 2 (3)	
Silver Nitrate	22.7 gm
Distilled water	163 ml

35

Solution 3 (3)	
Sodium Bromide	14.5 gm
Distilled water	164 ml

40

Solution 4 (3)	
Sodium Bromide	13.4 gm
Distilled water	127 ml

45

Solution 5 (3)	
Pluronic™ -31R1	1.0 gm
Distilled water	918 ml

50

55

EP 0 515 894 A1

Solution 6 (3)	
Silver Nitrate	1261 gm
Distilled water	4402 ml

Solution 7 (3)	
Sodium Bromide	798 gm
Distilled water	4414 ml

Solution 8 (3)	
Phthalated gelatin (bone)	255 gm
Distilled water	1600 ml

Solution 9 (3)	
Gelatin (bone)	123 gm
Distilled water	1660 ml

Solution 1 (3) was adjusted to a pH of 1.8 with nitric acid at 45° C. The pAg of solution 1 (3) was adjusted to pAg of 8.89 with sodium bromide. Solutions 2 (3) and 3 (3) were simultaneously run into solution 1 (3) at a constant rate for one minute and held for an additional minute when solution 4 (3) was added. The temperature of this mixture was adjusted to 60° C after which the mixture was treated with ammonium sulfate and sodium hydroxide to pH of 9.5 for 2 minutes. Solution 5 (3) was then added and the mixture was held for one minute. The pH was then adjusted to 5.8 with nitric acid. Simultaneous introduction of solutions 2 (3) and 3 (3) was resumed at a constant rate for 5 minutes while controlling pAg at 9.36. Solutions 6 (3) and 7 (3) were then introduced at an accelerated rate for 64 minutes and continued for 19 minutes at a constant rate. The pAg was controlled at 9.36 while solutions 6 (3) and 7 (3) were added. The temperature was then adjusted to 40° C and solution 8 (3) was added. After 5 minutes, the pH was adjusted to 3.5, the temperature reduced to 20° C and the mixture allowed to settle. When settling was complete, the liquid layer was decanted. The depleted volume was replaced with distilled water. The mixture was redispersed while the temperature was adjusted to 40° C and the pH adjusted to 5.5. The pH was adjusted to 3.5 and settling and decanting steps repeated. Solution 9 (3) was added, and the pH and pAg were adjusted to 5.5 and 8.2 respectively.

Emulsion 7B

A second emulsion (7B) was prepared like 7A with $K_4Fe(CN)_6$ at a formal concentration of 50 molar parts per million added in the salts from 1 to 70 percent of silver reagent addition, for an overall average concentration of 35 mppm based on silver.

Table VIII

Emulsion Characteristics				
Emulsion	equivalent circular diameter (ECD) (μm)	coefficient of ECD variation	thickness (μm)	grain volume (μm^3)
7A	1.45	10.6	0.12	0.22
7B	1.46	10.3	0.12	0.21

Example 8

Emulsions 5A, 5B, 5C and 5D were digested with 4 mg/mole of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 4 mg/mole of KAuCl_4 for 40 min. at 60 °C. Coatings were made at 21.5 mg Ag/dm^2 and of 53.8 mg gel/dm^2 . The coatings were given 0.1 sec exposures at 366 nm. The exposed coatings were developed for 6 min. in an hydroquinone-ElonTM (N,N-dimethylaminophenol hemisulfate) developer. The relative speed and fog levels are given in Table IX.

Example 9

Emulsions 5A, 5B, 5C and 5D were digested with 5 mg/mole of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 5 mg/mole of KAuCl_4 for 40 min. at 60 °C. Coatings were made at 21.5 mg Ag/dm^2 and of 53.8 mg gel/dm^2 . The coatings were given 0.1 sec exposures at 366 nm. The exposed coatings were developed for 6 min. in an elon-hydroquinone developer. The relative speed and fog levels are given in Table IX

Table IX

Emulsion	Example 8		Example 9	
	speed	fog	speed	fog
5A	100	0.04	100	0.04
5B	158	0.05	151	0.05
5C	186	0.06	178	0.06
5D	71	0.03	83	0.04

The examples given in Table IX clearly show speed advantages with the $\text{K}_4\text{Fe}(\text{CN})_6$ dopant, within the overall concentration range of the invention, but the overall concentration 175 mppm in Emulsion 5D was too high and resulted in a clear loss of speed.

Example 10

Emulsions 5A, 5B, 5C, 5D, 5E and 5F were digested with 4 mg/mole of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 4 mg/mole of KAuCl_4 , 150 mg/mole NaSCN , 20 mg/mole the finish modifier anhydro-5,6-dimethyl-3-(3-sulfopropyl)-benzothiazolium, inner salt (hereafter referred to as FM-1), and 400 mg/mole the spectral sensitizing dye anhydro-5,5'-dichloro-9-ethyl-3,3'-di(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt (hereafter referred to as S-1) for 40 min. at 60 °C. Three hundred mg/mole KI were added after finishing. Coatings were made at 21.5 mg Ag/dm^2 and of 53.8 mg gel/dm^2 . The coatings were given 0.1 sec exposures at 366 nm and from a 5500 °K light source with a Wratten-9TM filter (transmits at wavelengths longer than 490 nm). The exposed coatings were developed for 6 min. in a hydroquinone-ElonTM (N,N-dimethylaminophenol hemisulfate) developer. The relative speed and fog levels are given in Table X along with keeping data for 1 Week at 49 °C and 50% relative humidity. The keeping results are reported in terms of the change (delta) in log speed (DLS) and the change (delta) in minimum density (fog) (DF).

Table X

Emulsion	365nm speed	fog	5500 °K W9 speed	fog	Keeping DLS/DF
5A	100	0.04	100	0.04	+ 4/ +0.04
5B	126	0.05	151	0.05	-3/ +0.01
5C	135	0.06	162	0.06	-3/ +0.03
5D	5	0.03	<1	0.03	-
5E	126	0.05	158	0.05	-3/ +0.01
5F	100	0.05	120	0.05	-2/ +0.02

Speed and keeping advantages for dopant inclusion are clearly illustrated, except in Emulsion 5D, where dopant overall concentrations were clearly too high. The low contrast of Emulsion 5D due to its low speed made it impossible to measure accurately DLS or DF. In Emulsion 5E the same local maximum dopant

concentration was present as in Example 5D, but the overall concentration was within the range of the invention. Comparing Emulsions 5C and 5E, which contained the same overall dopant concentrations, with 5A a significant advantage was observed to result from distributing the dopant within the grain or having the dopant concentrated in a limited grain region so long as the overall dopant concentration was within the range of the invention. Emulsion 5F demonstrates that advantages can be realized with even very low concentrations of dopant.

Example 11

Emulsions 5A, 5B, 5C and 5E were digested with 4 mg/mole of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 4 mg/mole of KAuCl_4 for 40 min. at 60 ° C. Coatings were made at 21.5 mg Ag/dm² and of 53.8 mg gel/dm². Fifty percent of monomolecular layer coverage of spectral sensitizing dye anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt (hereafter referred to as S-2) was added after the finish. The coatings were given 0.1 sec exposures at 366 nm and from a 5500 ° K light source with a Wratten 9 TM filter. The exposed coatings were developed for 6 min. in an hydroquinone-Elon TM (N,N-dimethylaminophenol hemisulfate) developer. The relative speed and fog levels are given in Table XI.

Table XI

Emulsion	365nm		5500 ° K W9	
	speed	fog	speed	fog
5A	100	0.04	100	0.05
5B	141	0.05	141	0.06
5C	219	0.05	219	0.05
5E	87	0.05	158	0.05

By comparing Emulsion 5B containing 45 mppm dopant as an overall average with Emulsions 5C and 5E, each of which contained 35 mppm dopant as an overall average, based on silver, it is apparent that 35 mppm overall average dopant based on silver was superior. Further, comparing Emulsions 5C and 5E, it is apparent that the more nearly the maximum local dopant concentration approached the overall average, the better the results obtained.

Example 12

Emulsions 6A and 6B were digested with 4 mg/mole of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 4 mg/mole of KAuCl_4 , 150 mg/mole NaSCN, 20 mg/mole, finish modifier FM-1 and 400 mg/mole spectral sensitizing dye S-1 for 40 min. at 60 ° C. Three hundred mg/mole KI were added after finishing. Coatings were made at 21.5 mg Ag/dm² and 53.8 mg gel/dm². The coatings were given 0.1 sec exposures at 366 nm and from a tungston light source with filters to simulate a green emitting x-ray stimulated intensifying screen. The exposed coatings were developed for 6 min. in an hydroquinone-Elon TM (N,N-dimethylaminophenol hemisulfate)-developer. The data is given in table XII

Table XII

Emulsion	365nm		Gr Sc	
	speed	fog	speed	fog
6A	100	0.04	100	0.05
6B	126	0.05	115	0.05

Speed improvements are observed for the doped emulsion.

Example 13

Emulsions 7A and 7B were digested with 4 mg/mole of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, 4 mg/mole of KAuCl_4 , 150

mg/mole NaSCN, 20 mg/mole, finish modifier FM-1, and 400 mg/mole the spectral sensitizing dye S-1 for 40 min. at 60 ° C. Three hundred mg/mole KI were added after finishing. Coatings were made at 21.5 mg Ag/dm² and of 53.8 mg gel/dm². The coatings were given 0.1 sec exposures at 365 nm and from a 5500 ° K light source with a Wratten 9 TM filter. The exposed coatings were developed for 23 sec in a rapid access RP-X-OMAT TM processor with hydroquinone-ElonTM (N,N-dimethylaminophenol hemisulfate) developer. The data are given in Table XIII.

Table XIII

Emulsion	365nm		5500 ° K W9	
	speed	fog	speed	fog
7A	100	0.04	100	0.08
7B	151	0.04	123	0.08

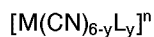
Speed improvements are observed for the doped emulsion.

Claims

1. A photographic emulsion comprised of a dispersing medium and silver bromide or silver bromiodide grains, at least 70 percent of the total projected area of the grains being accounted for by tabular grains having a thickness of less than 0.3 μm and a mean tabularity of greater than 25, the tabular grains having opposed parallel major faces and edge surfaces joining the parallel major faces of the tabular grains, characterized in that the opposed parallel major faces of the tabular grains lie in {111} crystallographic planes and less than 75 percent of the edge surfaces of said tabular grains lie in {111} crystallographic planes.
2. An emulsion according to claim 1 further characterized in that the tabular grains have a mean thickness of less than 0.2 μm .
3. An emulsion according to claim 1 or 2 further characterized in that the tabular grains account for greater than 90 percent of the total grain projected area.
4. An emulsion according to any one of claims 1 to 3 inclusive further characterized in that from 50 percent to less than 75 percent of the edge surfaces of said tabular grains lie in {111} crystallographic planes.
5. An emulsion according to any one of claims 1 to 4 inclusive further characterized in that the tabular grains are chemically sensitized and produce latent images adjacent their non-{111} edges.
6. An emulsion according to any one of claims 1 to 5 inclusive further characterized in that a spectral sensitizing dye is incorporated in the emulsion.
7. An emulsion according to claim 6 further characterized in that the spectral sensitizing dye is selectively adsorbed to the {111} crystal faces of the tabular grains.
8. An emulsion according to claim 7 further characterized in that the spectral sensitizing dye is adsorbed to the surfaces of the tabular grains in an amount sufficient to desensitize an emulsion in which greater than 75 percent of the edge surfaces lie in {111} crystallographic planes.
9. An emulsion according to any one of claims 1 to 8 inclusive further characterized in that the edge surfaces of the tabular grains are formed with edge surfaces lying in {111} and {100} crystallographic planes.
10. An emulsion according to any one of claims 1 to 9 inclusive further characterized in that the tabular grains contain a photographically useful amount of a hexacoordination complex of a group 8 metal and

at least three cyano ligands.

11. An emulsion according to claim 10 further characterized in that the tabular grains a hexacoordination complex satisfying the formula:



where

L is a bridging ligand,

M is Fe, Ru or Os,

y is the integer zero, 1, 2 or 3 and

n is -3 or -4.

12. An emulsion according to claim 10 or 11 further characterized in that the tabular grains contain from 1 to 150 molar parts per million of the hexacoordination complex based on silver.

13. An emulsion according to claim 12 further characterized in that the tabular grains contain from 30 to 100 molar parts per million of the hexacoordination complex based on silver.

14. An emulsion according to any one of claims 10 to 13 inclusive further characterized in that the hexacoordination complex contains iron as the group 8 metal, at least 3 cyano ligands, with any remaining ligands being halide ligands.

15. An emulsion according to claim 14 further characterized in that the tabular grains contain $[Fe(CN)_6]^{-4}$ in an amount of from 30 to 100 molar parts per million based on silver and with a maximum local concentration of less than 150 molar parts per million.

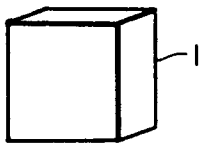


FIG. 1

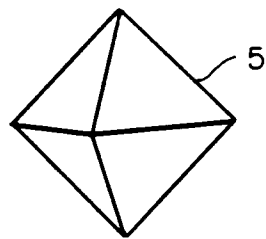


FIG. 3

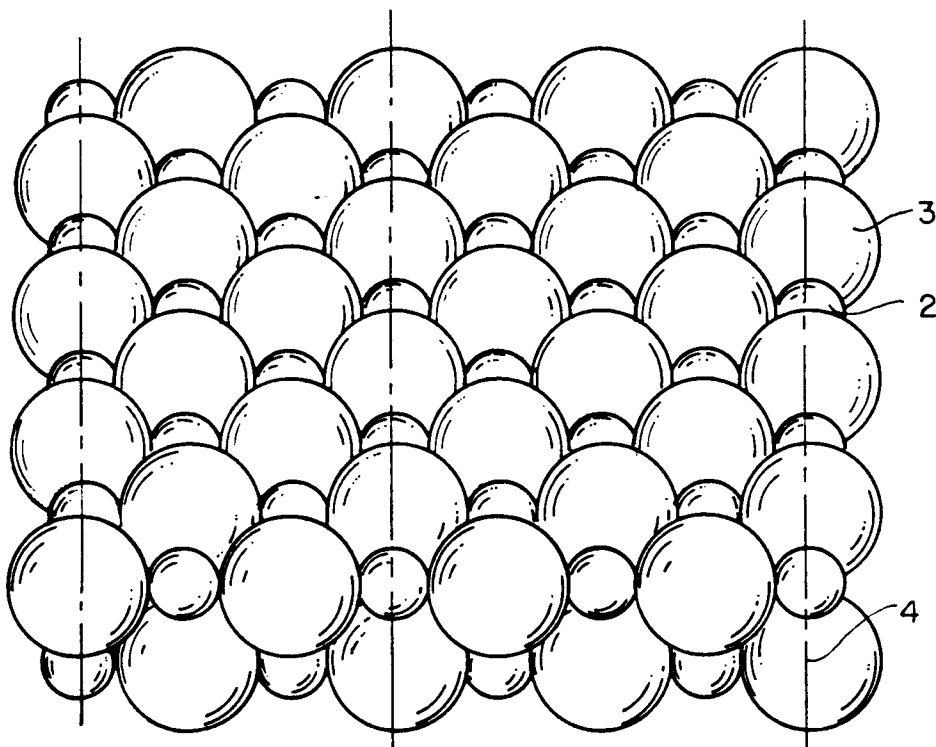


FIG. 2

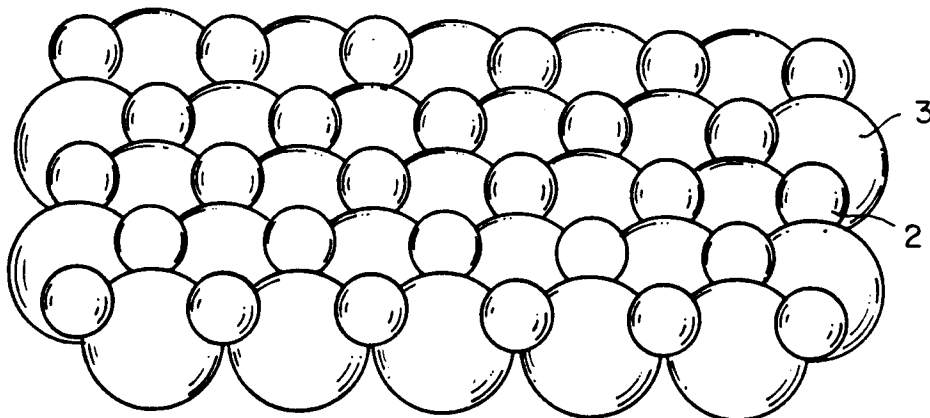


FIG. 4

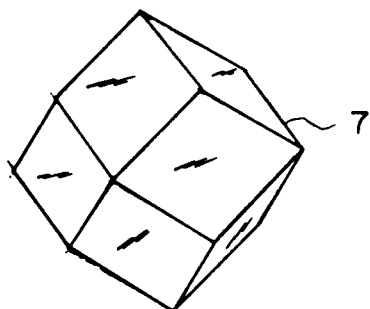


FIG. 5

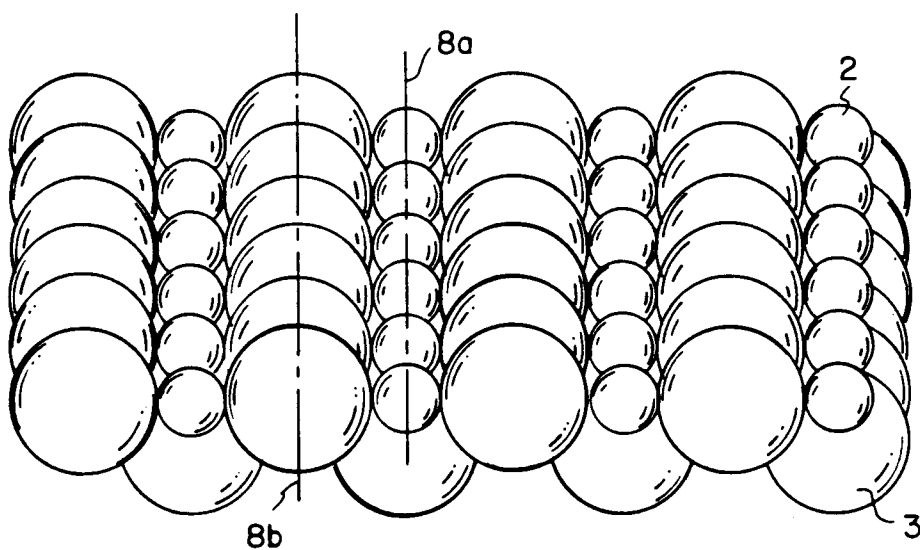


FIG. 6

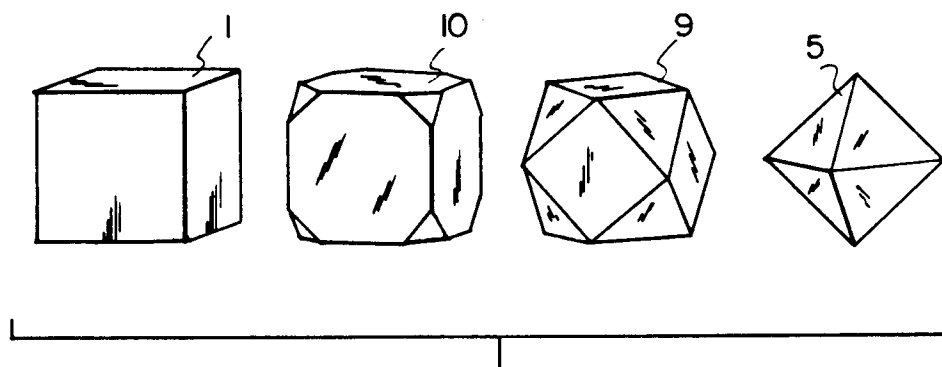


FIG. 7



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 7965

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	JOURNAL OF IMAGING SCIENCE, vol. 29, no. 5, September 1985, SPRINGFIELD US pages 165 - 171; T.TANI: 'Quantitative Determination of Crystal Habit of Silver Halide Grains Through Its Influence on Dye Adsorption' * the whole document *	1-15	G03C1/035 G03C1/08
A	EP-A-0 325 235 (FUJI PHOTO FILM COMPANY LTD.) * claims 1-20; examples 1,2 *	10-15	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09 SEPTEMBER 1992	Examiner BUSCHA A. J.
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			