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High aspect ratio photographic silver bromoiodide emulsions and process for their preparation

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(73) Proprietors
Eastman Kodak Company
(USA—New York)
343 State Street
Rochester
New York 14650
United States of America

(72) Inventors
John Anthony Haefner
Herbert Sedgwick Wilgus

(74) Agent and/or
Address for Service
P. A. C. Baron,
Kodak Limited,
Patents and Trade Marks Dept.,
Headstone Drive,
Harrow,
Middlesex HA1 4TY

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GB 1596602
GB 1570581
GB 1520976
GB 1469480

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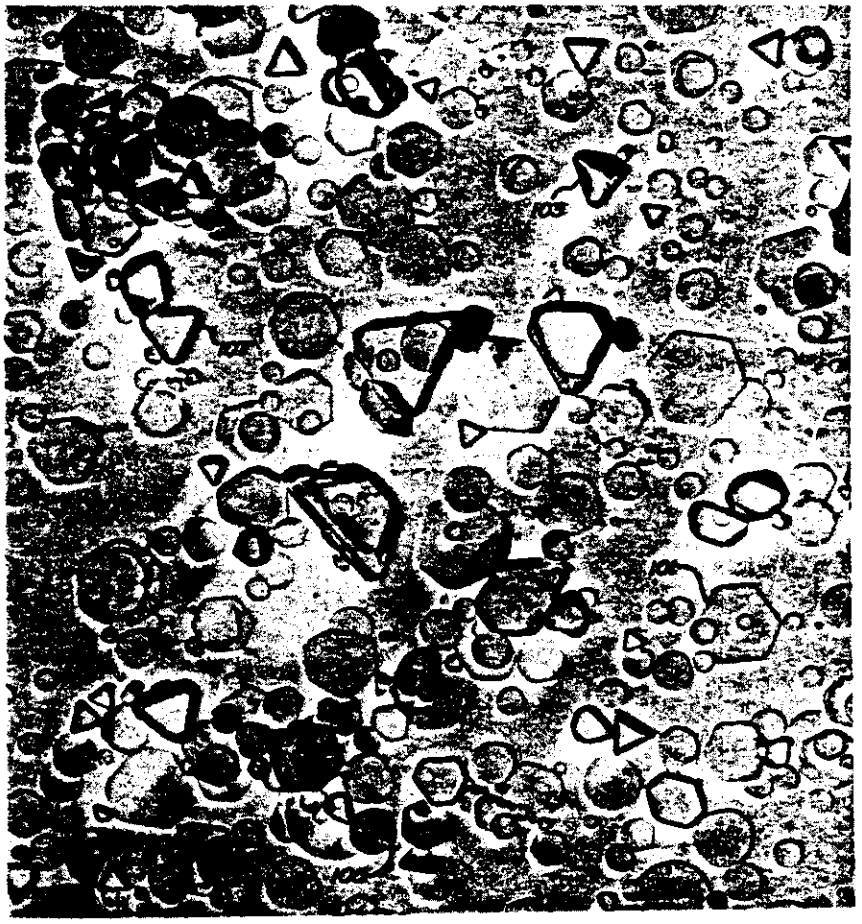


FIG. 1

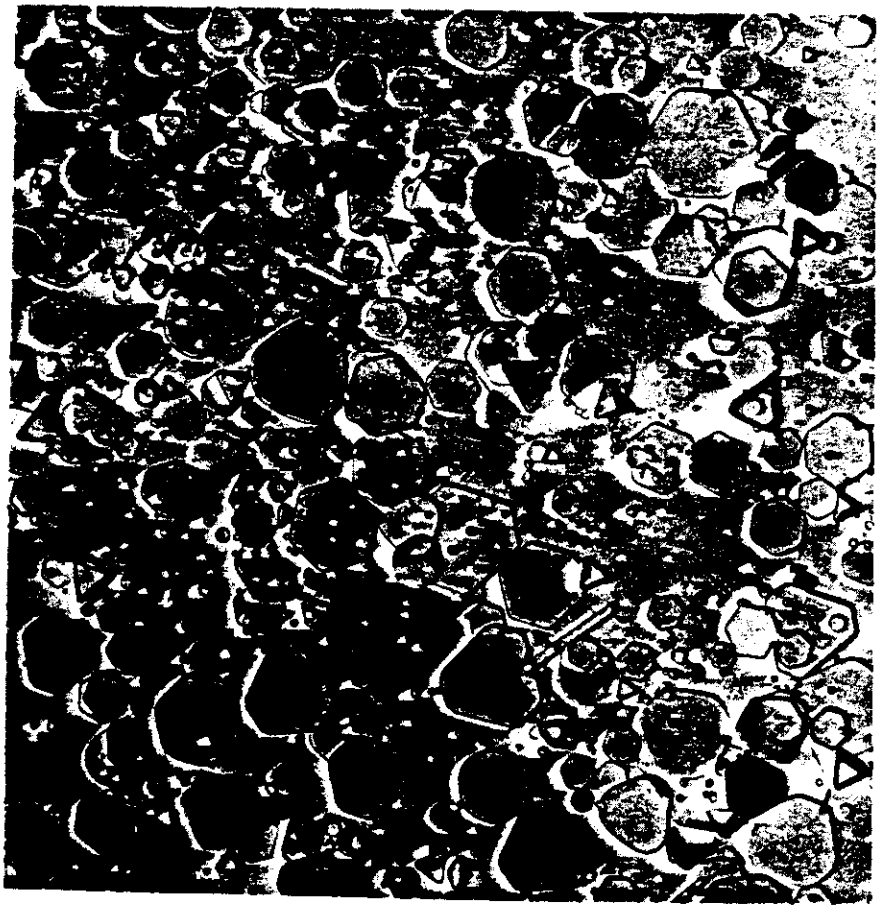
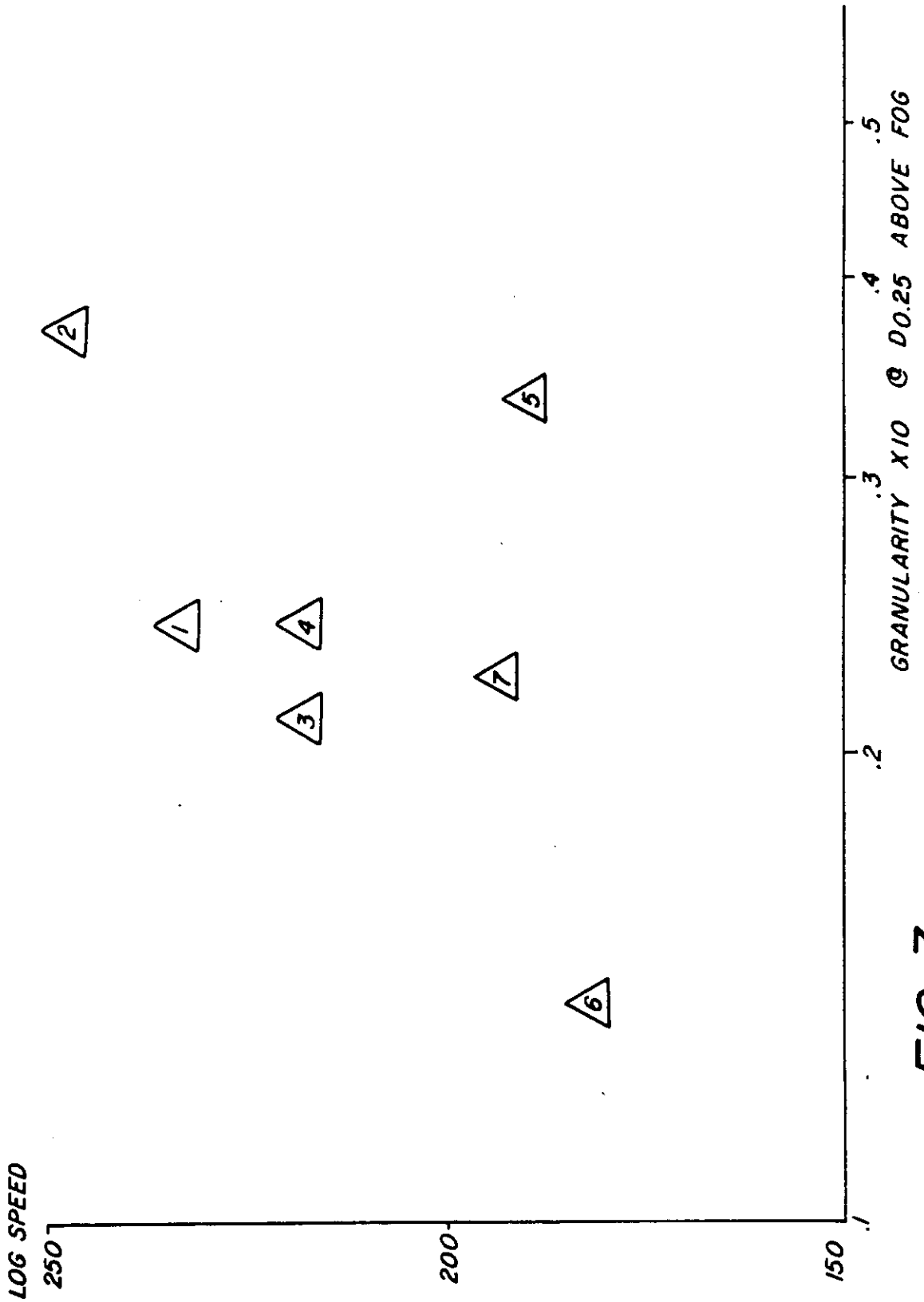


FIG. 2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.2
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6
7

FIG. 3

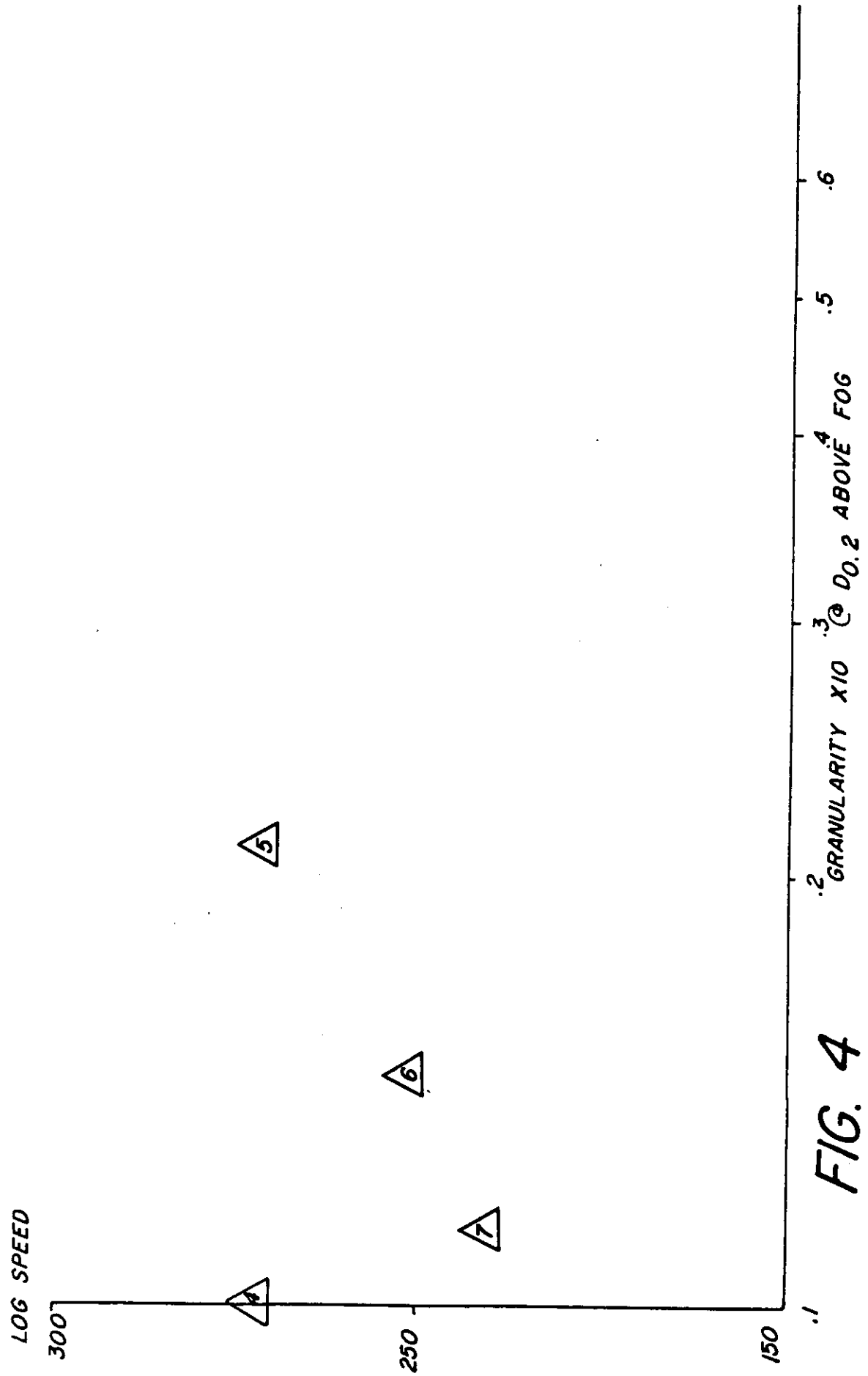
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FIG. 4

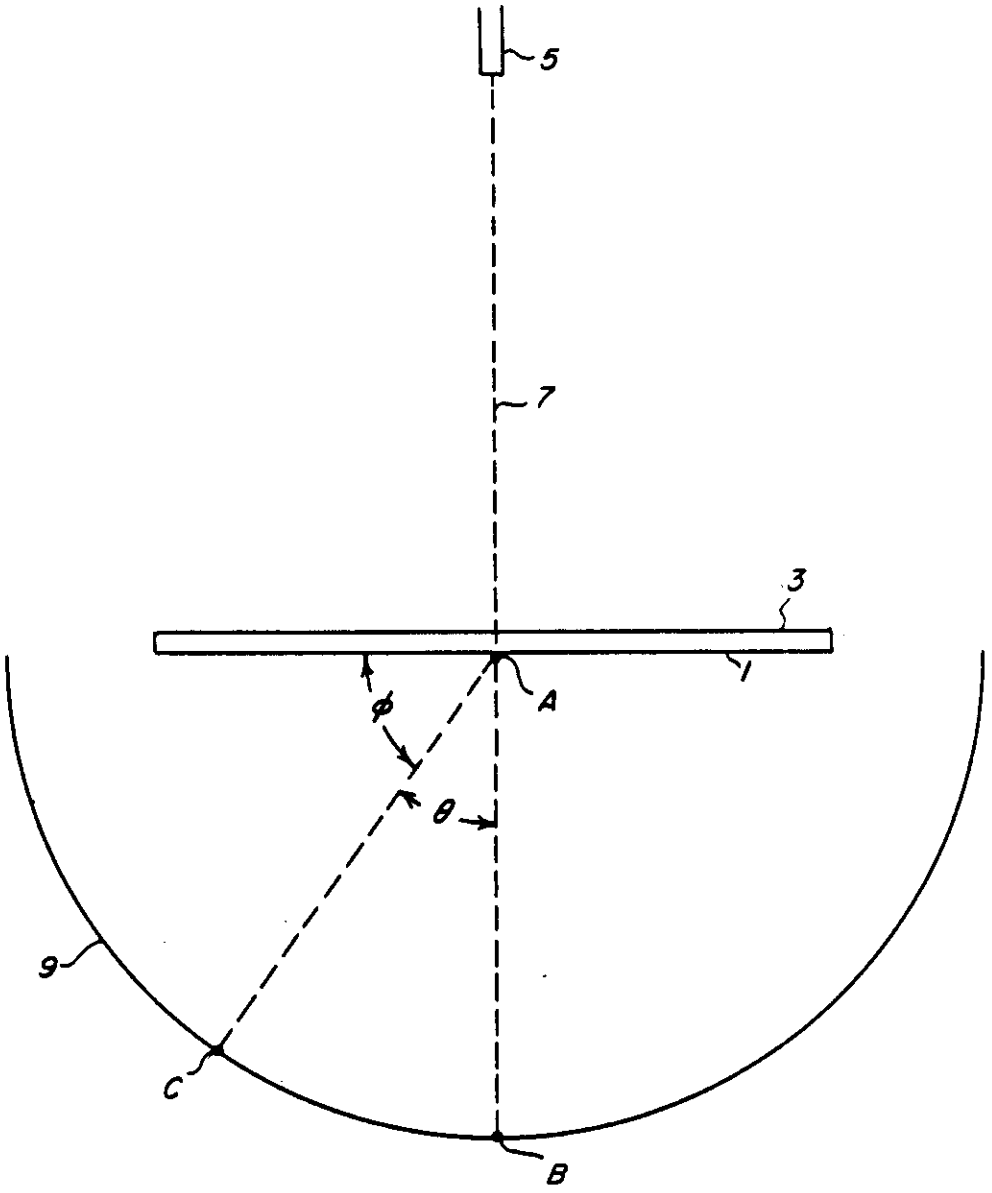

FIG. 5

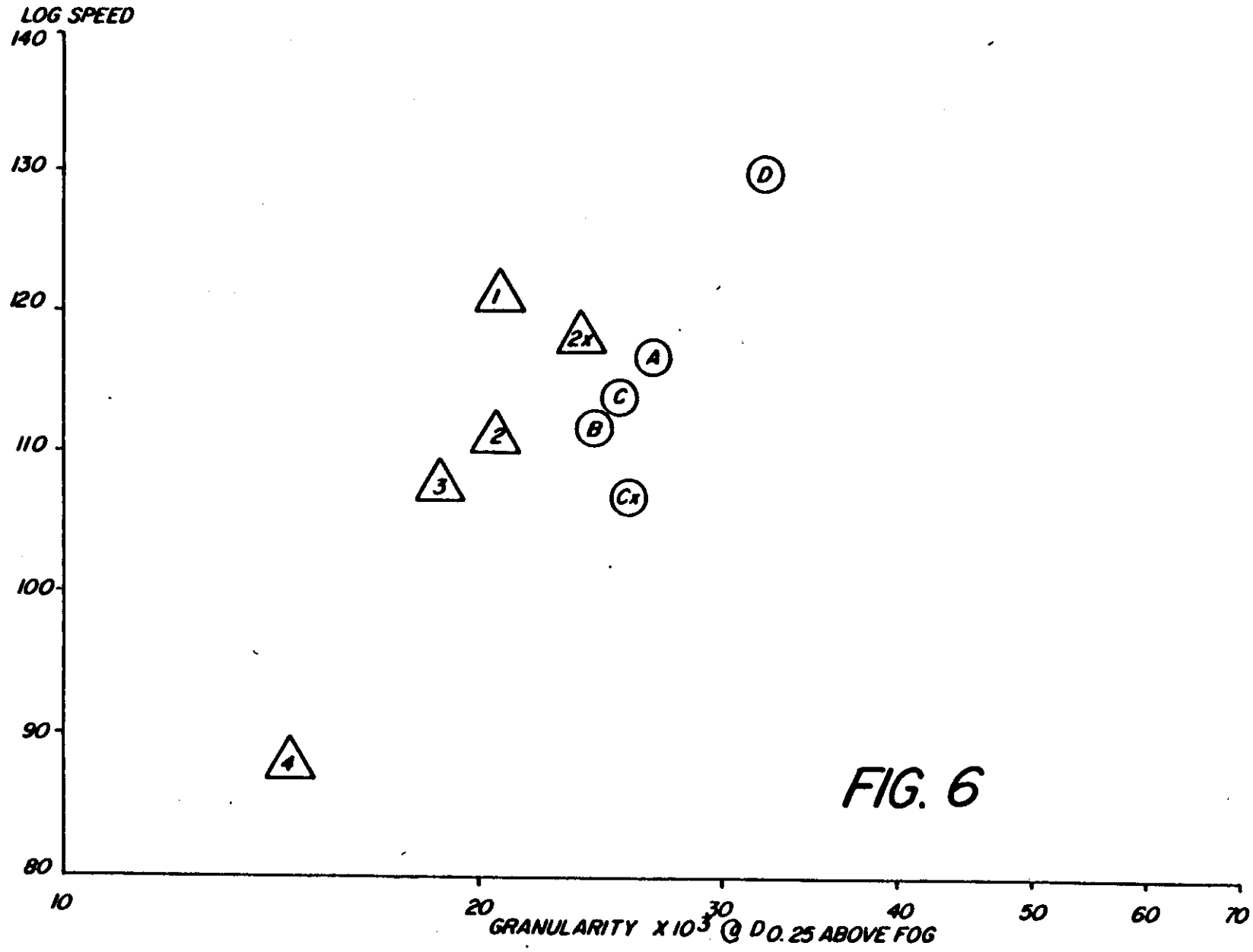

FIG. 6

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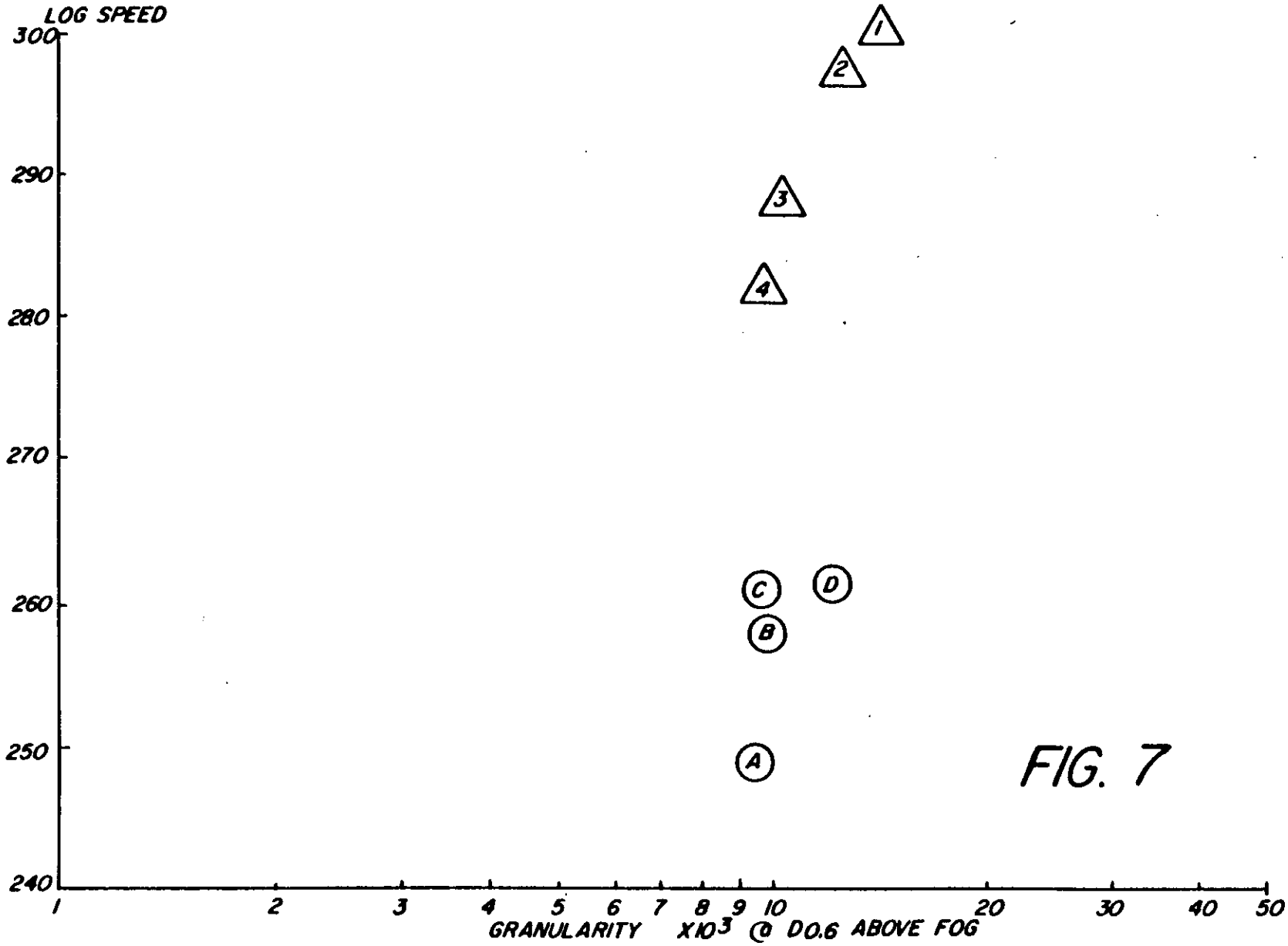

FIG. 7

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HIGH ASPECT RATIO PHOTOGRAPHIC SILVER BROMOIODIDE EMULSIONS AND PROCESS FOR THEIR PREPARATION

This invention relates to a photographic silver bromoiodide emulsion comprising a dispersing medium and tabular silver bromoiodide grains and to a process for its preparation.

Radiation-sensitive emulsions employed in photography are comprised of a dispersing medium, typically gelatin, containing embedded microcrystals --known as grains--of radiation-sensitive silver halide. Emulsions other than silver bromoiodide find only limited use in camera speed photographic elements. U.S. Patent 3,320,069 discloses gelatino-silver bromoiodide emulsions in which the iodide preferably comprises from 1 to 10 mole percent. Silver bromoiodide grains do not consist of some crystals of silver bromide and others of silver iodide. Rather, all of the crystals contain both bromide and iodide. Although it is possible to introduce silver iodide up to its solubility limit in silver bromide--that is, up to about 40 mole percent iodide, depending upon the temperature of grain formation, much lower iodide concentrations are usually employed. Except for specialized applications, silver bromoiodide emulsions seldom employ more than about 20 mole percent iodide. Even very small amounts of iodide, as low as 0.05 mole percent, can be beneficial. Except as otherwise indicated, all references to halide percentages are based on silver present in the corresponding emulsion, grain, or grain region being discussed; e.g., a grain consisting of silver bromoiodide containing 40 mole percent iodide also contains 60 mole percent bromide.

A great variety of regular and irregular grain shapes have been observed in silver halide photographic emulsions intended for black-and-white imaging applications generally and radiographic

imaging applications specifically. Regular grains are often cubic or octahedral. Grain edges can exhibit rounding due to ripening effects, and in the presence of strong ripening agents, such as ammonia, the grains may even be spherical or exist as thick platelets, which are nearly spherical as described, for example by Land U.S. Patent 3,894,871 and Zelikman and Levi Making and Coating Photographic Emulsions, Focal Press, 1964, page 223. Rods and tabular grains in varied portions have been frequently observed mixed in among other grain shapes, particularly where the pAg (the negative logarithm of silver ion concentration) of the emulsions has been varied during precipitation, as occurs, for example in single-jet precipitations.

Tabular silver bromide grains have been extensively studied, often in macro-sizes having no photographic utility. Tabular grains are herein defined as those having two parallel or substantially parallel crystal faces, each of which is substantially larger than any other single crystal face of the grain. The aspect ratio--that is, the ratio of diameter to thickness--of tabular grains is substantially greater than 1:1. High aspect ratio tabular grain silver bromide emulsions were reported by de Cugnac and Chateau, "Evolution of the Morphology of Silver Bromide Crystals During Physical Ripening", Science et Industries Photographiques, Vol. 33, No. 2 (1962), pp. 121-125.

From 1937 until the 1950's the Eastman Kodak Company sold a Duplitized (trade mark) radiographic film product under the name No-Screen X-Ray Code 5133. The product contained as coatings on opposite major faces of a film support sulfur sensitized silver bromide emulsions. Since the emulsions were intended

to be exposed by X-radiation, they were not spectrally sensitized. The tabular grains had an average aspect ratio in the range of from about 5 to 7:1. The tabular grains accounted for greater than 50% of the projected area while nontabular grains accounted for greater than 25% of the projected area. Upon reproducing these emulsions several times, the emulsion having the highest average aspect ratio has an average tabular grain diameter of 2.5 micrometers, an average tabular grain thickness of 0.36 micrometer, and an average aspect ratio of 7:1. In other remakes the emulsions contain thicker, smaller diameter tabular grains which are of lower average aspect ratio.

Although tabular grain silver bromoiodide emulsions are known in the art, none exhibit a high average aspect ratio. A discussion of tabular silver bromoiodide grains appears in Duffin, Photographic Emulsion Chemistry, Focal Press, 1966, pp. 66-72, and Trivelli and Smith, "The Effect of Silver Iodide Upon the Structure of Bromo-Iodide Precipitation Series", The Photographic Journal, Vol. LXXX, July 1940, pp. 285-288. Trivelli and Smith observed a pronounced reduction in both grain size and aspect ratio with the introduction of iodide. Gutoff, "Nucleation and Growth Rates During the Precipitation of Silver Halide Photographic Emulsions", Photographic Sciences and Engineering, Vol. 14, No. 4, July-August 1970, pp. 248-257, reports preparing silver bromide and silver bromoiodide emulsions of the type prepared by single-jet precipitations using a continuous precipitation apparatus.

Procedures for preparing emulsions in which a major proportion of the silver halide is present in the form of tabular grains have recently published. U.S. Patent 4,063,951 teaches forming silver halide crystals of tabular habit bounded by {100} cubic

faces and having an aspect ratio (based on edge length) of from 1.5 to 7:1. The tabular grains exhibit square and rectangular major surfaces characteristic of {100} crystal faces. U.S. Patent 4,067,739 teaches the preparation of silver halide emulsions wherein most of the crystals are of the twinned octahedral type by forming seed crystals, causing the seed crystals to increase in size by Ostwald ripening in the presence of a silver halide solvent, and completing grain growth without renucleation or Ostwald ripening while controlling pBr (the negative logarithm of bromide ion concentration). U.S. Patents 4,150,994, 4,184,877, and 4,184,878, U.K. Patent 1,570,581, and German OLS publications 2,905,655 and 2,921,077 teach the formation of silver halide grains of flat twinned octahedral configuration by employing seed crystals which are at least 90 mole percent iodide. U.S. Patent 4,063,951 specifically reports an upper limit on aspect ratios to 7:1, but, from the very low aspect ratio obtained by the example (2:1), the 7:1 aspect ratio appears unrealistically high. It is clear from repeating examples and viewing the photomicrographs published that the aspect ratios realized in the other above-mentioned references were also less than 7:1. Japanese patent Kokai 142,329, published November 6, 1980, appears to relate to similar subject matter as U.S. Patent 4,150,994, but is not restricted to the use of silver iodide as the seed grains.

According to the present invention there is provided a photographic silver bromoiodide emulsion comprising a dispersing medium and tabular silver bromoiodide grains which is characterized in that tabular silver bromoiodide grains having a thickness of less than 0.5 micrometer and a diameter of at least 0.6 micrometer have an average aspect ratio of greater

than 8:1 and account for at least 50% of the total projected area of the silver bromoiodide grains in the emulsion, aspect ratio being defined as the ratio of the diameter of a tabular grain to its thickness and the diameter of a grain being defined as the diameter of a circle having an area equal to the projected area of said grain.

The present invention also provides a process of preparing a photographic silver bromoiodide emulsion according to the present invention by introducing silver, bromide, and iodide salts into a reaction vessel containing at least a portion of the dispersing medium, characterized by

adjusting the pBr of the dispersing medium within the reaction vessel prior to introduction of the iodide salt to a level of from 0.6 to 1.6,

maintaining the reaction vessel substantially free of iodide prior to introduction of the silver and bromide salts, and

maintaining the pBr within the reaction vessel at a level of at least 0.6 during introduction of the iodide salts.

The above process for preparing the emulsion can, in one embodiment comprise introducing silver, bromide and iodide salts into a reaction vessel containing at least a portion of the dispersing medium for the emulsion to be prepared and is characterized by the steps of (1) adjusting the pBr of the dispersing medium within the reaction vessel to a level of from 1.6 to 0.6 prior to concurrent introduction of the silver, bromide and iodide salts, (2) maintaining the reaction vessel substantially free of iodide prior to said concurrent introduction of the silver, bromide and iodide salts, and (3) maintaining the pBr within the reaction vessel at a level of at least 0.6 during said concurrent introduction of the silver, bromide and iodide salts.

According to U.S. Patents 4,067,739 and 4,150,994 and other references referred to above,

silver halide emulsions of only low aspect ratios are provided. Advantages in covering power and other photographic characteristics are recognized therein. By preparing high aspect ratio silver bromoiodide emulsions the invention for the first time combines the known advantages of silver bromoiodide emulsions with the advantages of high aspect ratio.

Significant advantages in speed-granularity relationship, sharpness, blue sensitivity, and blue and minus blue (that is, green or red) sensitivity differences for chemically and spectrally sensitized high aspect ratio tabular grains silver bromoiodide emulsions according to this invention can be realized. The high aspect ratio tabular grain emulsions of this invention enhance sharpness of underlying emulsion layers when the tabular grain layers are positioned to receive light that is free of significant scattering. The emulsions of the present invention are particularly effective in this respect when they are located in the emulsion layers nearest the source of exposing radiation. When spectrally sensitized outside the blue portion of the spectrum, the emulsions of the present invention exhibit a large separation in their sensitivity in the blue region of the spectrum as compared to the region of the spectrum to which they are spectrally sensitized. Minus blue sensitized silver bromoiodide emulsions according to the invention are much less sensitive to blue light than to minus blue light and do not require filter protection to provide acceptable minus blue exposure records when exposed in neutral light, such as daylight at 5500°K. The silver bromoiodide emulsions of the present invention when sensitized exhibit improved speed-granularity relationships as compared to previously known tabular grain emulsions

and as compared to the best speed-granularity relationships heretofore achieved with silver bromoiodide emulsions generally. Very large increases in blue speed of the silver bromoiodide emulsions of the present invention have been realized as compared to their native blue speed when blue spectral sensitizers are employed.

Emulsions according to the present invention can be used in radiographic elements coated on both major surfaces of a radiation transmitting support to control crossover. Comparisons of radiographic elements containing emulsions according to this invention with similar radiographic elements containing conventional emulsions show that reduced crossover can be attributed to the emulsions of the present invention. Alternatively, comparable crossover levels can be achieved with the emulsions of the present invention using reduced silver coverages.

Emulsions according to the present invention can also be used in image transfer film units. The image transfer film units are capable of achieving a higher ratio of photographic speed to silver coverage (i.e., silver halide coated per unit area), faster access to a viewable transferred image, and higher contrast of transferred images with less time of development.

The silver bromoiodide emulsions of this invention can produce further photographic advantages, such as reduced sensitivity to variations in processing temperature and increased color contrast. Still other photographic advantages can be realized, depending upon the specific photographic application contemplated.

In addition the present invention offers an advantageous method of preparing emulsions of high aspect ratio silver bromoiodide grains. Although the

use of seed crystals is not incompatible with the practice of this invention, it is unnecessary either to provide seed crystals or to manipulate precipitation conditions between the nucleating and growth stages of emulsion precipitation in order to obtain grains of high aspect ratios. In its preferred form, the precipitation process of this invention can be manipulatively simpler than the prior art processes of obtaining tabular silver bromoiodide emulsions and superior in obtaining high aspect ratio tabular grain silver bromoiodide emulsions where other processes have failed.

Brief Description of the Drawings

Figures 1 and 2 are photomicrographs of emulsions according to the present invention,

Figures 3 and 4 are plots of speed versus granularity, and

Figure 5 is a schematic diagram related to scattering.

As applied to the silver bromoiodide emulsions of the present invention the term "high aspect ratio" is herein defined as requiring that the silver bromoiodide grains having a thickness of less than 0.5 and a diameter of at least 0.6 micrometer have an average aspect ratio of greater than 8:1 and account for at least 50 percent of the total projected area of the silver halide grains.

The preferred high aspect ratio tabular grain silver bromoiodide emulsions of the present invention are those wherein the silver bromoiodide grains having a thickness of less than 0.3 micrometer (optimally less than 0.2 micrometer) and a diameter of at least 0.6 micrometer have an average aspect ratio of at least 12:1 and optimally at least 20:1. Very high average aspect ratios (100:1 or even 200:1 or more) can be obtained. In a preferred form of the invention these silver bromoiodide grains account for

at least 70 percent and optimally at least 90 percent of the total projected area of the silver bromoiodide grains.

It is appreciated that the thinner the tabular grains accounting for a given percentage of the projected area, the higher the average aspect ratio of the grain. Typically the tabular grains have an average thickness of at least 0.03 micrometer, preferably at least 0.05 micrometer, although even thinner tabular grains can in principle be employed. In image transfer film units tabular grains having average thicknesses up to 0.5 micrometer can be used advantageously. Average grain thicknesses of up to 0.5 micrometer are also discussed below for recording blue light. However, to achieve high aspect ratios without unduly increasing grain diameters, it is normally contemplated that the tabular grains of the emulsions of this invention will have an average thickness of less than 0.3 micrometer.

The grain characteristics described above of the silver bromoiodide emulsions of this invention can be readily ascertained by procedures well known to those skilled in the art. As employed herein the term "aspect ratio" refers to the ratio of the diameter of the grain to its thickness. The "diameter" of the grain is in turn defined as the diameter of a circle having an area equal to the projected area of the grain as viewed in a photomicrograph or an electron micrograph of an emulsion sample. From shadowed electron micrographs of emulsion samples it is possible to determine the thickness and diameter of each grain and to identify those tabular grains having a thickness of less than 0.5, preferably 0.3, micrometer and a diameter of at least 0.6 micrometer. From this the aspect ratio of each such tabular grain can be calculated, and the aspect ratios of all the tabular grains in the sample meeting the

less than 0.5, preferably 0.3, micrometer thickness and at least 0.6 micrometer diameter criteria can be averaged to obtain their average aspect ratio. By this definition the average aspect ratio is the average of individual tabular grain aspect ratios. In practice it is usually simpler to obtain an average thickness and an average diameter of the tabular grains having a thickness of less than 0.5 micrometer and a diameter of at least 0.6 micrometer and to calculate the average aspect ratio as the ratio of these two averages. Whether the averaged individual aspect ratios or the averages of thickness and diameter are used to determine the average aspect ratio, within the tolerances of grain measurements contemplated, the average aspect ratios obtained do not significantly differ. The projected areas of the tabular silver bromoiodide grains meeting the thickness and diameter criteria can be summed, the projected areas of the remaining silver bromoiodide grains in the photomicrograph can be summed separately, and from the two sums the percentage of the total projected area of the silver bromoiodide grains provided by the tabular grains meeting the thickness and diameter critera can be calculated.

In the above determinations a reference tabular grain thickness of less than 0.5 micrometer was chosen to distinguish the uniquely thin tabular grains herein contemplated from thicker tabular grains which provide inferior photographic properties. A reference grain diameter of 0.6 micrometer was chosen, since at lower diameters it is not always possible to distinguish tabular and nontabular grains in micrographs. The term "projected area" is used in the same sense as the terms "projection area" and "projective area" commonly employed in the art; see, for example, James and Higgins, Fundamentals of Photographic Theory,

Morgan and Morgan, New York, p. 15.

Figure 1 is an exemplary photomicrograph of an emulsion according to the present invention chosen to illustrate the variant grains that can be present. Grain 101 illustrates a tabular grain that satisfies the thickness and diameter criteria set forth above. It is apparent that the vast majority of the grains present in Figure 1 are tabular grains which satisfy the thickness and diameter critera. These grains exhibit an average aspect ratio of 18:1. Also present in the photomicrograph are a few grains which do not satisfy the thickness and diameter critera. The grain 103, for example, illustrates a nontabular grain. It is of a thickness greater than 0.5 micrometer. The grain 105 illustrates a fine grain present that does not satisfy the diameter criterion. The grain 107 illustrates a thick tabular grain that satisfies the diameter criterion, but not the thickness criterion. Depending upon the conditions chosen for emulsion preparation, more specifically discussed below, in addition to the desired tabular silver bromoiodide grains satisfying the thickness and diameter criteria secondary grain populations of largely nontabular grains, fine grains, or thick tabular grains can be present. Occasionally other nontabular grains, such as rods, can be present. While it is generally preferred to maximize the number of tabular grains satisfying the thickness and diameter criteria, the presence of secondary grain populations is specifically contemplated, provided the emulsions remain of high aspect ratio, as defined above.

The high aspect ratio tabular grain silver bromoiodide emulsions can be prepared by a precipitation process which also forms a part of the present invention. Into a conventional reaction vessel for silver halide precipitation equipped with an efficient stirring mechanism is introduced a

dispersing medium. Typically the dispersing medium initially introduced into the reaction vessel is at least about 10 percent, preferably 20 to 80 percent, by weight, based on total weight of the dispersing medium present in the silver bromoiodide emulsion at the conclusion of grain precipitation. Since dispersing medium can be removed from the reaction vessel by ultrafiltration during silver bromoiodide grain precipitation, as taught by French Patent 2,471,620, corresponding to Belgian Patent 886,645, it is appreciated that the volume of dispersing medium initially present in the reaction vessel can equal or even exceed the volume of the silver bromoiodide emulsion present in the reaction vessel at the conclusion of grain precipitation. The dispersing medium initially introduced into the reaction vessel is preferably water or a dispersion of peptizer in water, optionally containing other ingredients, such as one or more silver halide ripening agents and/or metal dopants, more specifically described below. Where a peptizer is initially present, it is preferably employed in a concentration of at least 10 percent, most preferably at least 20 percent, of the total peptizer present at the completion of silver bromoiodide precipitation. Additional dispersing medium is added to the reaction vessel with the silver and halide salts and can also be introduced through a separate jet. It is common practice to adjust the proportion of dispersing medium, particularly to increase the proportion of peptizer, after the completion of the salt introductions.

A minor portion, typically less than 10 percent, by weight, of the bromide salt employed in forming the silver bromoiodide grains is initially present in the reaction vessel to adjust the bromide ion concentration of the dispersing medium at the outset of silver bromoiodide precipitation. Also, the dispersing medium in the reaction vessel is

initially substantially free of iodide ions, since the presence of iodide ions prior to concurrent introducton of silver and bromide salts favors the formation of thick and nontabular grains. As employed herein, the term "substantially free of iodide ions" as applied to the contents of the reaction vessel means that there are insufficient iodide ions present as compared to bromide ions to precipitate as a separate silver iodide phase. It is preferred to maintain the iodide concentration in the reaction vessel prior to silver salt introduction at less than 0.5 mole percent of the total halide ion concentration present. If the pBr of the dispersing medium is initially too high, the tabular silver bromoiodide grains produced will be comparatively thick and therefore of low aspect ratios. It is contemplated to maintain the pBr of the reaction vessel initially at or below 1.6, preferably below 1.5. On the other hand, if the pBr is too low, the formation of nontabular silver bromoiodide grains is favored. Therefore, it is contemplated to maintain the pBr of the reaction vessel at or above 0.6, preferably above 1.1. As herein employed, pBr is defined as the negative logarithm of bromide ion concentration. pH, pCl, pI, and pAg are similarly defined for hydrogen, chloride, iodide, and silver ion concentrations, respectively.

During precipitation silver, bromide, and iodide salts are added to the reaction vessel by techniques well known in the precipitation of silver bromoiodide grains. Typically an aqueous solution of a soluble silver salt, such as silver nitrate, is introduced into the reaction vessel concurrently with the introduction of the bromide and iodide salts. The bromide and iodide salts are also typically introduced as aqueous salt solutions, such as aqueous

solutions of one or more soluble ammonium, alkali metal (e.g., sodium or potassium), or alkaline earth metal (e.g., magnesium or calcium) halide salts. The silver salt is at least initially introduced into the reaction vessel separately from the iodide salt. The iodide and bromide salts can be added to the reaction vessel separately or as a mixture.

With the introduction of silver salt into the reaction vessel the nucleation stage of grain formation is initiated. A population of grain nuclei is formed which is capable of serving as precipitation sites for silver bromide and silver iodide as the introduction of silver, bromide, and iodide salts continues. The precipitation of silver bromide and silver iodide onto existing grain nuclei constitutes the growth stage of grain formation. The aspect ratios of the tabular grains formed according to this invention are less affected by iodide and bromide concentrations during the growth stage than during the nucleation stage. It is therefore possible during the growth stage to increase the permissible latitude of pBr during concurrent introduction of silver, bromide, and iodide salts above 0.6, preferably in the range of from 0.6 to 2.2, most preferably from 0.8 to 1.6, the latter being particularly preferred where a substantial rate of grain nuclei formation continues throughout the introduction of silver, bromide, and iodide salts, such as in the preparation of highly polydispersed emulsions. Raising pBr values above 2.2 during tabular grain growth results in thickening of the grains, but can be tolerated in many instances while still realizing an average aspect ratio of greater than 8:1.

As an alternative to the introduction of silver, bromide, and iodide salts as aqueous

solutions, it is specifically contemplated to introduce the silver, bromide, and iodide salts, initially or in the growth stage, in the form of fine silver halide grains suspended in dispersing medium. The grain size is such that they are readily Ostwald ripened onto larger grain nuclei, if any are present, once introduced into the reaction vessel. The maximum useful grain sizes will depend on the specific conditions within the reaction vessel, such as temperature and the presence of solubilizing and ripening agents. Silver bromide, silver iodide, and/or silver bromoiodide grains can be introduced. Since bromide and/or iodide are precipitated in preference to chloride, it is also possible to employ silver chlorobromide and silver chlorobromoiodide grains. The silver halide grains are preferably very fine--e.g., less than 0.1 micrometer in mean diameter.

Subject to the pBr requirements set forth above, the concentrations and rates of silver, bromide, and iodide salt introductions can take any convenient conventional form. The silver and halide salts are preferably introduced in concentrations of from 0.1 to 5 moles per liter, although broader conventional concentration ranges, such as from 0.01 mole per liter to saturation, for example, are contemplated. Specifically preferred precipitation techniques are those which achieve shortened precipitation times by increasing the rate of silver and halide salt introduction during the run. The rate of silver and halide salt introduction can be increased either by increasing the rate at which the dispersing medium and the silver and halide salts are introduced or by increasing the concentrations of the silver and halide salts within the dispersing medium being introduced. It is specifically preferred to increase the rate of silver and halide salt introduction, but to maintain the rate of introduction

below the threshold level at which the formation of new grain nuclei is favored--i.e., to avoid renucleation, as taught by U.S. Patents 3,650,757; 3,672,900; 4,242,445; German OLS 2,107,118, European Patent Application 80102242, and Wey "Growth Mechanism of AgBr Crystals in Gelatin Solution", Photographic Science and Engineering, Vol. 21, No. 1, January/ February 1977, p. 14, et. seq. By avoiding the formation of additional grain nuclei after passing into the growth stage of precipitation, relatively monodispersed tabular silver bromoiodide grain populations can be obtained. Emulsions having coefficients of variation of less than about 30 percent can be prepared employing the process of the present invention. As employed herein the coefficient of variation is defined as 100 times the standard deviation of the grain diameter divided by the average grain diameter. By intentionally favoring renucleation during the growth stage of precipitation, it is, of course, possible to produce polydispersed emusions of substantially higher coefficients of variation.

The concentration of iodide in the silver bromoiodide emulsions of this invention can be controlled by the introduction of iodide salts. Any conventional iodide concentration can be employed. Even very small amounts of iodide--e.g., as low as 0.05 mole percent--are recognized in the art to be beneficial. In their preferred form the emulsions of the present invention incorporate at least about 0.1 mole percent iodide. Silver iodide can be incorporated into the tabular silver bromoiodide grains up to its solubility limit in silver bromide at the temperature of grain formation. Thus, silver iodide concentrations of up to about 40 mole percent in the tabular silver bromoiodide grains can be achieved at

precipitation temperatures of 90°C. In practice precipitation temperatures can range down to near ambient room temperatures--e.g., about 30°C. It is generally preferred that precipitation be undertaken at temperatures in the range of from 40 to 80°C. For most photographic applications it is preferred to limit maximum iodide concentrations to about 20 mole percent, with optimum iodide concentrations being up to about 15 mole percent.

The relative proportion of iodide and bromide salts introduced into the reaction vessel during precipitation can be maintained in a fixed ratio to form a substantially uniform iodide profile in the tabular silver bromoiodide grains, or varied to achieve differing photographic effects. Specific photographic advantages result from increasing the proportion of iodide in annular regions of high aspect ratio tabular grain silver bromoiodide emulsions as compared to central regions of the tabular grains. Iodide concentrations in the central regions of the tabular grains can range from 0 to 5 mole percent, with at least one mole percent higher iodide concentrations in the laterally surrounding annular regions up to the solubility limit of silver iodide in silver bromide, preferably up to about 20 mole percent and optimally up to about 15 mole percent. In a variant form it is specifically contemplated to terminate iodide or bromide and iodide salt addition to the reaction vessel prior to the termination of silver salt addition so that excess halide reacts with the silver salt. This results in a shell of silver bromide being formed on the tabular silver bromoiodide grains. Thus, it is apparent that the tabular silver bromoiodide grains of the present invention can exhibit substantially uniform or graded iodide concentration profiles and

that the gradation can be controlled, as desired, to favor higher iodide concentrations internally or at or near the surfaces of the tabular silver bromoiodide grains.

Modifying compounds can be present during silver bromoiodide precipitation. Such compounds can be initially in the reaction vessel or can be added along with one or more of the salts according to conventional procedures. Modifying compounds, such as compounds of copper, thallium, lead, bismuth, cadmium, zinc, middle chalcogens (i.e., sulfur, selenium and tellurium), gold, and Group VIII noble metals, can be present during silver halide precipitation, as illustrated by U.S. Patents 1,195,432; 1,951,933; 2,448,060; 2,628,167; 2,950,972; 3,488,709; 3,737,313; 3,772,031; 4,269,927; and Research Disclosure, Vol. 134, June 1975, Item 13452. Research Disclosure and its predecessor, Product Licensing Index, are publications of Industrial Opportunities Ltd.; Homewell, Havant; Hampshire, P09 1EF, United Kingdom. The tabular grain emulsions can be internally reduction sensitized during precipitation, as illustrated by Moisar et al, Journal of Photographic Science, Vol. 25, 1977, pp. 19-27.

The individual silver and halide salts can be added to the reaction vessel through surface or subsurface delivery tubes by gravity feed or by delivery apparatus for maintaining control of the rate of delivery and the pH, pBr, and/or pAg of the reaction vessel contents, as illustrated by U.S. Patents 3,821,002 and 3,031,304 and Claes et al, Photographische Korrespondenz, Band 102, Number 10, 1967, p. 162. In order to obtain rapid distribution of the reactants within the reaction vessel, specially constructed mixing devices can be employed,

as illustrated by U.S. Patents 2,996,287; 3,342,605; 3,415,650; 3,785,777; 4,147,551; 4,171,224; U.K. Patent Application 2,022,431A; German OLS 2,555,364 and 2,556,885, and Research Disclosure, Volume 166, February 1978, Item 16662.

In forming the tabular grain silver bromoiodide emulsions a dispersing medium is initially contained within the reaction vessel. In a preferred form the dispersing medium is comprised of an aqueous peptizer suspension. Peptizer concentrations of from 0.2 to 10 percent by weight, based on the total weight of emulsion components in the reaction vessel, can be employed. It is common practice to maintain the concentration of the peptizer in the reaction vessel below about 6 percent, based on the total weight, prior to and during silver halide formation and to adjust the emulsion vehicle concentration upwardly for optimum coating characteristics by delayed, supplemental vehicle additions. It is contemplated that the emulsion as initially formed will contain from 5 to 50 grams of peptizer per mole of silver halide, preferably 10 to 30 grams of peptizer per mole of silver halide. Additional vehicle can be added later to bring the concentration up to as high as 1000 grams per mole of silver halide. Preferably the concentration of vehicle in the finished emulsion is above 50 grams per mole of silver halide. When coated and dried in forming a photographic element the vehicle preferably forms 30 to 70 percent by weight of the emulsion layer.

Vehicles (which include both binders and peptizers) can be chosen from among those conventionally employed in silver halide emulsions. Preferred peptizers are hydrophilic colloids, which can be employed alone or in combination with hydrophobic

materials. Suitable hydrophilic materials include substances such as proteins, protein derivatives, cellulose derivatives--e.g., cellulose esters, gelatin--e.g., alkali-treated gelatin (cattle bone or hide gelatin) or acid-treated gelatin (pigskin gelatin), gelatin derivatives--e.g., acetylated gelatin, phthalated gelatin. These and other vehicles are disclosed in Research Disclosure, Vol. 176, December 1978, Item 17643, Section IX. The vehicle materials, including particularly the hydrophilic colloids, as well as the hydrophobic materials useful in combination therewith can be employed not only in the emulsion layers of the photographic elements of this invention, but also in other layers, such as overcoat layers, interlayers and layers positioned beneath the emulsion layers.

It is specifically contemplated that grain ripening can occur during the preparation of silver bromoiodide emulsions according to the present invention. Known silver halide solvents are useful in promoting ripening. For example, an excess of bromide ions, when present in the reaction vessel, is known to promote ripening. It is therefore apparent that the bromide salt solution run into the reaction vessel can itself promote ripening. Other ripening agents can also be employed and can be entirely contained within the dispersing medium in the reaction vessel before silver and halide salt addition, or they can be introduced into the reaction vessel along with one or more of the halide salt, silver salt, or peptizer. In still another variant the ripening agent can be introduced independently during halide and silver salt additions. Although ammonia is a known ripening agent, it is not a preferred ripening agent for the silver bromoiodide emulsions of this invention exhibiting the highest

realized speed-granularity relationships. The preferred emulsions of the present invention are non-ammoniacal or neutral emulsions.

Among preferred ripening agents are those containing sulfur. Thiocyanate salts can be used, such as the alkali metal salts, most commonly sodium and potassium thiocyanate salts , and ammonium thiocyanate salts. While any conventional quantity of the thiocyanate salts can be introduced, preferred concentrations are generally from 0.1 to 20 grams of thiocyanate salt per mole of silver halide. Illustrative prior teachings of employing thiocyanate ripening agents are found in U.S. Patent 2,222,264, cited above; U.S. Patents 2,448,534 and 3,320,069. Alternatively, conventional thioether ripening agents, such as those disclosed in U.S. Patents 3,271,157; 3,574,628; and 3,737,313, can be employed.

The high aspect ratio tabular grain silver bromoiodide emulsions of the present invention are preferably washed to remove soluble salts. The soluble salts can be removed by well-known techniques, such as by decantation, filtration, and/or chill setting and leaching, as illustrated by Research Disclosure, Vol. 176, December 1978, Item 17643, Section II. In the present invention washing is particularly advantageous in terminating ripening of the tabular silver bromoiodide grains after the completion of precipitation to avoid increasing their thickness and reducing their aspect ratio. The emulsions, with or without sensitizers, can be dried and stored prior to use.

Although the preparation of the high aspect ratio tabular grain silver bromoiodide emulsions has been described by reference to the process of the present invention, which produces neutral or nonammoniacal emulsions, the emulsions of the present

invention and their utility are not limited by any particular process for their preparation. According to an alternative process a radiation-sensitive tabular grain silver bromoiodide emulsion according to the present invention can be prepared by a method comprising (a) providing in a reaction vessel an emulsion comprising a dispersing medium and high iodide silver halide grains, and (b) concurrently introducing into the reaction vessel silver and bromide salts, wherein the mean diameter of said high iodide grains is limited to less than 0.1 micron and the concentration of iodide is limited to less than 10^{-2} mole per liter, before the silver and bromide salts are concurrently introduced.

Once the high aspect ratio tabular grain emulsions have been formed by the process of the present invention they can be shelled to produce a core-shell emulsion by procedures well known to those skilled in the art. Any photographically useful silver salt can be employed in forming shells on the high aspect ratio tabular grain emulsions prepared by the present process. Techniques for forming silver salt shells are illustrated by U.S. Patents 3,367,778; 3,206,313; 3,317,322; and 4,150,994. Since conventional techniques for shelling do not favor the formation of high aspect ratio tabular grains, as shell growth proceeds the average aspect ratio of the emulsion declines. If conditions favorable for tabular grain formation are present in the reaction vessel during shell formation, shell growth can occur preferentially on the outer edges of the grains so that aspect ratio need not decline. High aspect ratio core-shell tabular grain emulsions are particularly useful for producing internal latent images and can be used in forming either negative working or direct reversal photographic elements.

Although the procedures for preparing tabular silver halide grains described above will produce high aspect ratio tabular grain emulsions in

which the tabular grains satisfying the thickness and diameter criteria for aspect ratio account for at least 50 percent of the total projected area of the total silver halide grain population, it is recognized that further advantages can be realized by increasing the proportion of such tabular grains present. Preferably at least 70 percent (optimally at least 90 percent) of the total projected area is provided by tabular silver halide grains meeting the thickness and diameter criteria. While minor amounts of nontabular grains are fully compatible with many photographic applications, to achieve the full advantages of tabular grains the proportion of tabular grains can be increased. Larger tabular silver halide grains can be mechanically separated from smaller, nontabular grains in a mixed population of grains using conventional separation techniques--e.g., by using a centrifuge or hydrocyclone. An illustrative teaching of hydrocyclone separation is provided by U.S. Patent 3,326,641.

The high aspect ratio tabular grain emulsions of the present invention can be chemically sensitized. They 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, rhodium, rhenium, or phosphorus sensitizers or combinations of these sensitizers, such as at pAg levels of from 5 to 10, pH levels of from 5 to 8 and temperatures of from 30 to 80°C, as illustrated by Research Disclosure, Vol. 120, April 1974, Item 12008, Research Disclosure, Vol. 134, June 1975, Item 13452, U.S. Patents 1,623,499; 1,673,522; 2,399,083; 2,642,361; 3,297,447; 3,297,446; U.K. Patent 1,315,755; U.S. Patents 3,772,031; 3,761,267; 3,857,711; 3,565,633; 3,901,714 and 3,904,415 and U.K. Patent 1,396,696; chemical sensitization being

optionally conducted in the presence of thiocyanate compounds, as described in U.S.Patent 2,642,361; sulfur containing compounds of the type disclosed in U.S. Patents 2,521,926; 3,021,215 and 4,054,457. It is specifically contemplated to sensitize chemically in the presence of finish (chemical sensitization) modifiers--that is, compounds known to suppress fog and increase speed when present during chemical sensitization, such as azaindenes, azapyridazines, azapyrimidines, benzothiazolium salts, and sensitizers having one or more heterocyclic nuclei. Exemplary finish modifiers are described in U.S. Patent 2,131,038; 3,411,914; 3,554,757; 3,565,631; 3,901,714; Canadian Patent 778,723, and Duffin Photographic Emulsion Chemistry, Focal Press (1966), New York, pp. 138-143. Additionally or alternatively, the emulsions can be reduction sensitized--e.g., with hydrogen, as illustrated by U.S. Patents 3,891,446 and 3,984,249, by low pAg (e.g., less than 5) and/or high pH (e.g., greater than 8) treatment or through the use of reducing agents, such as stannous chloride, thiourea dioxide, polyamines and amine-boranes, as illustrated by U.S. Patent 2,983,609, Research Disclosure, Vol. 136, August 1975, Item 13654, U.S. Patents 2,518,698; 2,739,060; 2,743,182 and 2,743,183; 3,026,203; and 3,361,564. Surface chemical sensitization, including sub-surface sensitization, illustrated by U.S. Patents 3,917,485 and 3,966,476, is specifically contemplated.

In addition to being chemically sensitized the high aspect ratio tabular grain silver bromoiodide emulsions of the present invention can also be spectrally sensitized. It is specifically contemplated to employ spectral sensitizing dyes that exhibit absorption maxima in the blue and minus blue--i.e., green and/or red, portions of the visible spectrum. In addition, for specialized applications, spectral sensitizing dyes can be employed which

improve spectral response beyond the visible spectrum. For example, the use of infrared absorbing spectral sensitizers is specifically contemplated.

The emulsions of this invention can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines (i.e., tri-, tetra- and poly-nuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls and streptocyanines.

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, benz[e]indolium, oxazolium, oxazolinium, thiazolium, thiazolinium, selenazolium, selenazolinium, imidazolium, imidazolinium, benzoxazolium, benzothiazolium, benzoselenazolium, benzimidazolium, naphthoxazolium, naphthothiazolium, naphthoselenazolium, dihydronaphthothiazolium, pyrylium, and imidazopyrazinium quaternary salts.

The merocyanine spectral sensitizing dyes include, joined by a double bond or methine linkage, a basic heterocyclic nucleus of the cyanine dye type and an acidic nucleus, such as can be derived from barbituric acid, 2-thiobarbituric acid, rhodanine, hydantoin, 2-thiohydantoin, 4-thiohydantoin, 2-pyrazolin-5-one, 2-isoxazolin-5-one, indan-1,3-dione, cyclohexanel,3-dione, 1,3-dioxane-4,6-dione, pyrazolin-3,5- dione, pentane-2,4-dione, alkylsulfonylacetonitrile, malononitrile, isoquinolin-4-one, and chroman-2,4- dione.

One or more spectral sensitizing dyes may be used. Dyes with sensitizing maxima at wavelengths throughout the visible 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 for 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 between the sensitizing maxima of the individual dyes.

Combinations of spectral sensitizing dyes can be used which result in supersensitization--that is, spectral sensitization that is 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, "Review of the Mechanisms of Supersensitization", Photographic Science and Engineering, Vol. 18, 1974, pp. 418-430.

Spectral sensitizing dyes also affect the emulsions in other ways. Spectral sensitizing dyes can also function as antifoggants or stabilizers, development accelerators or inhibitors, and halogen acceptors or electron acceptors, as disclosed in U.S. Patents 2,131,038 and 3,930,860.

Among useful spectral sensitizing dyes for sensitizing silver bromoiodide emulsions are those referred to in Research Disclosure, Vol. 176, December 1978, Item 17643, Section III.

To realize the full advantages of this invention it is preferred to adsorb spectral sensitizing dye to the grain surfaces of the high aspect ratio tabular grain silver bromoiodide emulsions of this invention in an optimum amount--that is, in an amount sufficient to realize at least 60 percent of the maximum photographic speed attainable from the grains under contemplated conditions of exposure. The quantity of dye employed will vary with the specific dye or dye combination chosen as well as the size and aspect ratio of the grains. It is known in the photographic art that optimum spectral sensitization is obtained with organic dyes at about 25 to 100 percent or more of monolayer coverage of the total available surface area of surface sensitive silver halide grains, as disclosed, for example, in West et al, "The Adsorption of Sensitizing Dyes in Photographic Emulsions", Journal of Phys. Chem., Vol 56, p. 1065, 1952; Spence et al, "Desensitization of Sensitizing Dyes", Journal of Physical and Colloid Chemistry, Vol. 56, No. 6, June 1948, pp. 1090-1103; and U.S. Patent 3,979,213. Optimum dye concentration levels can be chosen by procedures taught by Mees, Theory of the Photographic Process, 1942, Macmillan, pp. 1067-1069. Although native blue sensitivity of silver bromoiodide is commonly relied upon in the art in emulsion layers intended to record exposure to blue light, significant advantages can be obtained by the use of blue spectral sensitizers.

Spectral sensitization can be undertaken at any stage of emulsion preparation heretofore known to be useful. Most commonly spectral sensitization is undertaken in the art subsequent to the completion of chemical sensitization. However, it is specifically recognized that spectral sensitization can be undertaken alternatively concurrently with chemical

sensitization, can entirely precede chemical sensitization, and can even commence prior to the completion of silver halide grain precipitation, as taught by U.S. Patents 3,628,960; and 4,225,666. As taught by U.S. Patent 4,225,666, it is specifically contemplated to distribute introduction of the spectral sensitizing dye into the emulsion so that a portion of the spectral sensitizing dye is present prior to chemical sensitization and a remaining portion is introduced after chemical sensitization. Unlike U.S. Patent 4,225,666, it is specifically contemplated that the spectral sensitizing dye can be added to the emulsion after 80 percent of the silver halide has been precipitated. Sensitization can be enhanced by pAg adjustment, including variation in pAg which completes one or more cycles during chemical and/or spectral sensitization. A specific example of pAg adjustment is provided by Research Disclosure, Vol. 181, May 1979, Item 18155.

High aspect ratio tabular grain silver bromoiodide emulsions can exhibit higher speed-granularity relationships when chemically and spectrally sensitized than have been heretofore realized using silver bromoiodide emulsions containing low aspect ratio tabular grains and/or exhibiting the highest known speed-granularity relationships. Best results have been achieved using minus blue spectral sensitizing dyes.

In one preferred form, spectral sensitizers can be incorporated in the emulsions of the present invention prior to chemical sensitization. Similar results have also been achieved in some instances by introducing other adsorbable materials, such as finish modifiers, into the emulsions prior to chemical sensitization.

Independent of the prior incorporation of adsorbable materials, it is preferred to employ thiocyanates during chemical sensitization in concentrations of from about 2×10^{-3} to 2 mole percent, based on silver, as taught by U.S. Patent 2,642,361, cited above. Other ripening agents can be used during chemical sensitization.

In still a third approach, which can be practiced in combination with one or both of the above approaches or separately thereof, it is preferred to adjust the concentration of silver and/or halide salts present immediately prior to or during chemical sensitization. Soluble silver salts, such as silver acetate, silver trifluoroacetate, and silver nitrate, can be introduced as well as silver salts capable of precipitating onto the grain surfaces, such as silver thiocyanate, silver phosphate, silver carbonate, and the like. Fine silver halide (i.e., silver bromide, iodide, and/or chloride) grains capable of Ostwald ripening onto the tabular grain surfaces can be introduced. For example, a Lippmann emulsion can be introduced during chemical sensitization. The chemical sensitization of spectrally sensitized high aspect ratio tabular grain emulsions can be effected at one or more ordered discrete sites of the tabular grains. It is believed that the preferential adsorption of spectral sensitizing dye on the crystallographic surfaces forming the major faces of the tabular grains allows chemical sensitization to occur selectively at unlike crystallographic surfaces of the tabular grains.

The preferred chemical sensitizers for the highest attained speed-granularity relationships are gold and sulfur sensitizers, gold and selenium sensitizers, and gold, sulfur, and selenium sensitizers. Thus, in a preferred form of the

invention, the high aspect ratio tabular grain silver bromoiodide emulsions of the present invention contain a middle chalcogen, such as sulfur and/or selenium, which may not be detectable, and gold, which is detectable. The emulsions also usually contain detectable levels of thiocyanate, although the concentration of the thiocyanate in the final emulsions can be greatly reduced by known emulsion washing techniques. In various of the preferred forms indicated above the tabular silver bromoiodide grains can have another silver salt at their surface, such as silver thiocyanate, or another silver halide of differing halide content, (e.g. silver chloride, or silver bromide), although the other silver salt may be present below detectable levels.

Although not required to realize all of their advantages, the emulsions of the present invention are preferably, in accordance with prevailing manufacturing practices, optimally chemically and spectrally sensitized. That is, they preferably achieve speeds of at least 60 percent of the maximum log speed attainable from the grains in the spectral region of sensitization under the contemplated conditions of use and processing. Log speed is herein defined as 100 (1-log E), where E is measured in meter-candle-seconds at a density of 0.1 above fog. Once the silver halide grain content of an emulsion has been characterized it is possible to estimate from further product analysis and performance evaluation whether an emulsion layer of a product appears to be optimally chemically and spectrally sensitized in relation to comparable commercial offerings of other manufacturers. To achieve the sharpness advantages of the present invention it is immaterial whether the silver halide emulsions are chemically or spectrally sensitized efficiently or inefficiently.

Once high aspect ratio tabular grain emulsions have been generated by precipitation procedures, washed, and sensitized, as described above, their preparation can be completed by the incorporation of conventional photographic addenda, and they can be usefully applied to photographic applications requiring a silver image to be produced--e.g., conventional black-and-white photography.

Photographic elements having emulsions according to the present invention intended to form silver images can be hardened to an extent sufficient to obviate the necessity of incorporating additional hardener during processing. This permits increased silver covering power to be realized as compared to photographic elements similarly hardened and processed, but employing nontabular or less than high aspect ratio tabular grain emulsions. Specifically, it is possible to harden the high aspect ratio tabular grain emulsion layers and other hydrophilic colloid layers of black-and-white photographic elements in an amount sufficient to reduce swelling of the layers to less than 200 percent, percent swelling being determined by (a) incubating the photographic element at 38°C for 3 days at 50 percent relative humidity, (b) measuring layer thickness, (c) immersing the photographic element in distilled water at 21°C for 3 minutes, and (d) measuring change in layer thickness. Although hardening of the photographic elements intended to form silver images to the extent that hardeners need not be incorporated in processing solutions is specifically preferred, it is recognized that the emulsions of the present invention can be hardened to any conventional level. It is further specifically contemplated to incorporate hardeners in processing solutions, as

illustrated, for example, by Research Disclosure, Vol. 184, August 1979, Item 18431, Paragraph K, relating particularly to the processing of radiographic materials.

Typical useful incorporated hardeners (forehardeners) are illustrated in Research Disclosure, Vol. 176, December 1978, Item 17643, Section X.

Instability which increases minimum density in negative type emulsion coatings (i.e., fog) or which increases minimum density or decreases maximum density in direct-positive emulsion coatings 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 are illustrated in Research Disclosure, Vol. 176, December 1978, Item 17643, Section VI. Many of the antifoggants which are effective in emulsions 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.

Where hardeners of the aldehyde type are employed, the emulsion layers can be protected with conventional antifoggants.

In addition to sensitizers, hardeners, and antifoggants and stabilizers, a variety of other conventional photographic addenda can be present. The specific choice of addenda depends upon the exact nature of the photographic application and is well within the capability of the art. A variety of useful addenda are disclosed in Research Disclosure, Vol. 176, December 1978, Item 17643. Optical brighteners can be introduced, as disclosed by Item 17643 at Paragraph V. Absorbing and scattering

materials can be employed in the emulsions of the invention and in separate layers of the photographic elements, as described in Paragraph VIII. Coating aids, as described in Paragraph XI, and plasticizers and lubricants, as described in Paragraph XII, can be present. Antistatic layers, as described in Paragraph XIII, can be present. Methods of addition of addenda are described in Paragraph XIV. Matting agents can be incorporated, as described in Paragraph XVI. Developing agents and development modifiers can, if desired, be incorporated, as described in Paragraphs XX and XXI. When the photographic elements of the invention are intended to serve radiographic applications, emulsion and other layers of the radiographic element can take any of the forms specifically described in Research Disclosure, Item 18431, cited above. The emulsions of the invention, as well as other, conventional silver halide emulsion layers, interlayers, overcoats, and subbing layers, if any, present in the photographic elements can be coated and dried as described in Research Disclosure, Vol. 176, December 1978, Item 17643, Paragraph XV.

In accordance with established practices within the art it is specifically contemplated to blend the high aspect ratio tabular grain emulsions of the present invention with each other or with conventional emulsions to satisfy specific emulsion layer requirements. For example, it is known to blend emulsions to adjust the characteristic curve of a photographic element to satisfy a predetermined aim. Blending can be employed to increase or decrease maximum densities realized on exposure and processing, to decrease or increase minimum density, and to adjust characteristic curve shape between their toe and shoulder portions. To accomplish this the emulsions of this invention can be blended with

conventional silver halide emulsions, such as those described in Research Disclosure, Vol. 176, December 1978, Item 17643, cited above, Paragraph I. It is specifically contemplated to blend the emulsions as described in sub-paragraph F of Paragraph I. When a relatively fine grain silver chloride emulsion is blended with or coated adjacent the emulsions of the present invention, a further increase in the sensitivity--i.e., speed-granularity relationship--of the emulsion can result, as taught by U.S. Patents 3,140,179 and 3,152,907.

In their simplest form photographic elements according to the present invention employ a single emulsion layer containing a high aspect ratio tabular grain silver bromoiodide emulsion according to the present invention and a photographic support. It is, of course, recognized that more than one silver halide emulsion layer as well as overcoat, subbing, and interlayers can be usefully included. Instead of blending emulsions as described above the same effect can usually by achieved by coating the emulsions to be blended as separate layers. Coating of separate emulsion layers to achieve greater exposure latitude is well known in the art, as illustrated by Zelikman and Levi, Making and Coating Photographic Emulsions, Focal Press, 1964, pp. 234-238; U.S. Patent 3,662,228; and U.K. Patent 923,045. It is further well known in the art that increased photographic speed can be realized when faster and slower emulsions are coated in separate layers as opposed to blending. Typically the faster emulsion layer is coated to lie nearer the exposing radiation source than the slower emulsion layer. This approach can be extended to three or more superimposed emulsion layers. Such layer arrangements are specifically contemplated in the practice of this invention.

The layers of the photographic elements can be coated on a variety of supports. Typical photographic supports include polymeric film, wood fiber--e.g., paper, metallic sheet and foil, glass and ceramic supporting elements provided with one or more subbing layers to enhance the adhesive, antistatic, dimensional, abrasive, hardness, frictional, antihalation and/or other properties of the support surface. These supports are well known in the art; see for example, Research Disclosure, Vol. 176, December 1978, Item 17643, Section XVII.

Although the emulsion layer or layers are typically coated as continuous layers on supports having opposed planar major surfaces, this need not be the case. The emulsion layers can be coated as laterally displaced layer segments on a planar support surface. When the emulsion layer or layers are segmented, it is preferred to employ a microcellular support. Useful microcellular supports are disclosed by Patent Cooperation Treaty published application W080/01614, published August 7, 1980, (Belgian Patent 881,513, August 1, 1980, corresponding), and U.S. Patent 4,307,165. Microcells can range from 1 to 200 micrometers in width and up to 1000 micrometers in depth. It is generally preferred that the microcells be at least 4 micrometers in width and less than 200 micrometers in depth, with optimum dimensions being about 10 to 100 micrometers in width and depth for ordinary black-and-white imaging applications-- particularly where the photographic image is intended to be enlarged.

The photographic elements of the present invention can be imagewise exposed in any conventional manner. Attention is directed to Research Disclosure Item 17643, cited above, Paragraph XVIII. The present invention is

particularly advantageous when imagewise exposure is undertaken with electromagnetic radiation within the region of the spectrum in which the spectral sensitizers present exhibit absorption maxima. When the photographic elements are intended to record blue, green, red, or infrared exposures, spectral sensitizer absorbing in the blue, green, red, or infrared portion of the spectrum is present. For black-and- white imaging applications it is preferred that the photographic elements be orthochromatically or panchromatically sensitized to permit light to extend sensitivity within the visible spectrum. Radiant energy employed for exposure can be either noncoherent (random phase) or coherent (in phase), produced by lasers. Imagewise exposures at ambient, elevated or reduced temperatures and/or pressures, including high or low intensity exposures, continuous or intermittent exposures, exposure times ranging from minutes to relatively short durations in the millisecond to microsecond range and solarizing exposures, can be employed within the useful response ranges determined by conventional sensitometric techniques, as illustrated by T. H. James, The Theory of the Photographic Process, 4th Ed., Macmillan, 1977, Chapters 4, 6, 17, 18, and 23.

The light-sensitive silver halide contained in the photographic elements can be processed conventionally following exposure to form a visible image by associating the silver halide with an aqueous alkaline medium in the presence of a developing agent contained in the medium or the element.

Once a silver image has been formed in the photographic element, it is conventional practice to fix the undeveloped silver halide. The high aspect ratio tabular grain emulsions of the present

invention are particularly advantageous in allowing fixing to be accomplished in a shorter time period. This allows processing to be accelerated.

The photographic elements and the techniques described above for producing silver images can be readily adapted to provide a colored image through the use of dyes. In perhaps the simplest approach to obtaining a projectable color image a conventional dye can be incorporated in the support of the photographic element, and silver image formation undertaken as described above. In areas where a silver image is formed the element is rendered substantially incapable of transmitting light therethrough, and in the remaining areas light is transmitted corresponding in color to the color of the support. In this way a colored image can be readily formed. The same effect can also be achieved by using a separate dye filter layer or dye filter element together with an element having a transparent support element.

The silver halide photographic elements can be used to form dye images therein through the selective destruction or formation of dyes. The photographic elements described above for forming silver images can be used to form dye images by employing developers containing dye image formers, such as color couplers, as in Research Disclosure, Vol. 176, December 1978, Item 17643, Section XIX, Paragraph D. In this form the developer contains a color-developing agent (e.g., a primary aromatic amine) which in its oxidized form is capable of reacting with the coupler (coupling) to form the image dye.

Dye-forming couplers alternatively can be incorporated in the photographic elements in a conventional manner. They can be incorporated in

different amounts to achieve differing photographic effects. For example, in faster and intermediate speed emulsion layers the concentration of coupler in relation to the silver coverage can be limited to less than normally employed amounts in faster and intermediate speed emulsion layers.

The dye-forming couplers are commonly chosen to form subtractive primary (i.e., yellow, magenta and cyan) image dyes and are nondiffusible, colorless couplers. Dye-forming couplers of differing reaction rates in single or separate layers can be employed to achieve desired effects for specific photographic applications.

The dye-forming couplers upon coupling can release photographically useful fragments, such as development inhibitors or accelerators, bleach accelerators, developing agents, silver halide solvents, toners, hardeners, fogging agents, antifoggants, competing couplers, chemical or spectral sensitizers and desensitizers. Development inhibitor- releasing (DIR) couplers are well known in the art. So are dye-forming couplers and nondye-forming compounds which upon coupling release a variety of photographically useful groups. DIR compounds which do not form dye upon reaction with oxidized color-developing agents can also be employed. DIR compounds which oxidatively cleave can also be employed. Silver halide emulsions which are relatively light insensitive, such as Lippmann emulsions, have been utilized as interlayers and overcoat layers to prevent or control the migration of development inhibitor fragments.

The photographic elements can incorporate colored dye-forming couplers, such as those employed to form integral masks for negative color images and/or competing couplers. The photographic elements

can include image dye stabilizers. All of the above is disclosed in Research Disclosure, Vol. 176, December 1978, Item 17643, Section VII.

Dye images can be formed or amplified by processes which employ in combination with a dye-image-generating reducing agent an oxidizing agent in the form of an oxidizing agent in the form of an inert transition metal ion complex. The photographic elements can be particularly adapted to form dye images by such processes.

The photographic elements can produce dye images through the selective destruction of dyes or dye precursors, such as silver-dye-bleach processes. It is common practice in forming dye images in silver halide photographic elements to remove the developed silver by bleaching. Such removal can be enhanced by incorporation of a bleach accelerator or a precursor thereof in a processing solution or in a layer of the element. In some instances the amount of silver formed by development is small in relation to the amount of dye produced, particularly in dye image amplification, as described above, and silver bleaching is omitted without substantial visual effect. In still other applications the silver image is retained and the dye image is intended to enhance or supplement the density provided by the image silver. In the case of dye enhanced silver imaging it is usually preferred to form a neutral dye or a combination of dyes which together produce a neutral image. It is also possible to form monochromatic or neutral dye images using only dyes, silver being entirely removed from the image-bearing photographic elements by bleaching and fixing.

The present invention can be employed to produce multicolor photographic images. Generally any conventional multicolor imaging element

containing at least one silver halide emulsion layer can be improved merely by adding or substituting a high aspect ratio tabular grain emulsion according to the present invention. The present invention is fully applicable to both additive multicolor imaging and subtractive multicolor imaging.

To illustrate the application of this invention to additive multicolor imaging, a filter array containing interlaid blue, green, and red filter elements can be employed in combination with a photographic element according to the present invention capable of producing a silver image. A high aspect ratio tabular grain emulsion of the present invention which is panchromatically sensitized and which forms a layer of the photographic element is imagewise exposed through the additive primary filter array. After processing to produce a silver image and viewing through the filter array, a multicolor image is seen. Such images are best viewed by projection. Hence both the photographic element and the filter array both have or share in common a transparent support.

Significant advantages can be realized by the application of this invention to multicolor photographic elements which produce multicolor images from combinations of subtractive primary imaging dyes. Such photographic elements are comprised of a support and typically at least a triad of superimposed silver halide emulsion layers for separately recording blue, green, and red exposures as yellow, magenta, and cyan dye images, respectively.

In a specific preferred form a minus blue sensitized high aspect ratio tabular grain silver bromoiodide emulsion according to the invention forms at least one of the emulsion layers intended to record green or red light in a triad of blue, green,

and red recording emulsion layers of a multicolor photographic element. The tabular grain emulsion is positioned to receive during exposure of the photographic element to neutral light at 5500°K blue light in addition to the light the emulsion is intended to record. The relationship of the blue and minus blue light the layer receives can be expressed in terms of Δ log E, where

$$\Delta \log E = \log E_T - \log E_B$$

$\log E_T$ being the log of exposure to green or red light the tabular grain emulsion is intended to record and

$\log E_B$ being the log of concurrent exposure to blue light the tabular grain emulsion also receives. In each occurrence exposure, E, is in meter-candle-seconds, unless otherwise indicated.

Δ log E can be a positive value less than 0.7 (preferably less than 0.3) while still obtaining acceptable image replication of a multicolor subject. This is surprising in view of the high proportion of grains present in the emulsions of the present invention having an average diameter of greater than 0.7 micrometer. If a comparable nontabular or lower aspect ratio tabular grain emulsion of like halide composition and average grain diameter is substituted for a high aspect ratio tabular grain silver bromoiodide emulsion of the present invention a higher and usually unacceptable level of color falsification will result. In a specific preferred form of the invention at least the minus blue recording emulsion layers are silver bromoiodide emulsions according to the present invention. It is specifically contemplated that the blue recording emulsion layer of the triad can advantageously also be a high aspect ratio tabular grain emulsion according to the present invention.

In a specific preferred form of the invention the tabular grains present in each of the emulsion layers of the triad having a thickness of less than 0.3 micrometer have an average grain diameter of at least 1.0 micrometer, preferably at least 2 micrometers. In a still further preferred form of the invention the multicolor photographic elements can be assigned an ISO speed index of at least 180.

The multicolor photographic elements need contain no yellow filter layer positioned between the exposure source and the high aspect ratio tabular grain green and/or red emulsion layers to protect these layers from blue light exposure, or the yellow filter layer, if present, can be reduced in density to less than any yellow filter layer density heretofore employed to protect from blue light exposure red or green recording emulsion layers of photographic elements intended to be exposed in daylight. In one specifically preferred form no blue recording emulsion layer is interposed between the green and/or red recording emulsion layers of the triad and the source of exposing radiation. Therefore the photographic element is substantially free of blue absorbing material between the green and/or red emulsion layers and incident exposing radiation.

Although only one green or red recording high aspect ratio tabular grain silver bromoiodide emulsion as described above is required, the multicolor photographic element contains at least three separate emulsions for recording blue, green, and red light, respectively. The emulsions other than the required high aspect ratio tabular grain green or red recording emulsion can be of any convenient conventional form. Various conventional emulsions are illustrated by Research Disclosure, Item 17643, cited

above, Paragraph I. In a preferred form all of the emulsion layers contain silver bromoiodide grains. In a particularly preferred form at least one green recording emulsion layer and at least one red recording emulsion layer is comprised of a high aspect ratio tabular grain emulsion according to this invention. If more than one emulsion layer is provided to record in the green and/or red portion of the spectrum, it is preferred that at least the faster emulsion layer contain high aspect ratio tabular grain emulsion as described above. It is, of course, recognized that all of the blue, green, and red recording emulsion layers of the photographic element can advantageously be tabular grain emulsions according to this invention, if desired.

The present invention is fully applicable to multicolor photographic elements as described above in which the speed and contrast of the blue, green, and red recording emulsion layers vary widely. The relative blue insensitivity of green or red spectrally sensitized high aspect ratio tabular grain silver bromoiodide emulsion layers according to this invention allow green and/or red recording emulsion layers to be positioned at any location within a multicolor photographic element independently of the remaining emulsion layers and without taking any conventional precautions to prevent their exposure by blue light.

The present invention is particularly useful with multicolor photographic elements intended to replicate colors accurately when exposed in daylight. Photographic elements of this type are characterized by producing blue, green, and red exposure records of substantially matched contrast and limited speed variation when exposed to a 5500°K (daylight) source. The term "substantially matched

contrast" as employed herein means that the blue, green, and red records differ in contrast by less than 20 (preferably less than 10) percent, based on the contrast of the blue record. The limited speed variation of the blue, green, and red records can be expressed as a speed variation (Δ log E) of less than 0.3 log E, where the speed variation is the larger of the differences between the speed of the green or red record and the speed of the blue record.

Both contrast and log speed measurements necessary for determining these relationships of the photographic elements can be determined by exposing a photographic element at a color temperature of 5500°K through a spectrally nonselective (neutral density) step wedge, such as a carbon test object, and processing the photographic element, preferably under the processing conditions contemplated in use. By measuring the blue, green, and red densities of the photographic element to transmission of blue light of 435.8 nm in wavelength, green light of 546.1 nm in wavelength, and red light of 643.8 nm in wavelength, as described by American Standard PH2.1-1952, published by American National Standards Institute (ANSI), 1430 Broadway, New York, N.Y. 10018, blue, green, and red characteristic curves can be plotted for the photographic element. If the photographic element has a reflective support rather than a transparent support, reflection densities can be substituted for transmission densities. From the blue, green, and red characteristic curves speed and contrast can be ascertained by procedures well known to those skilled in the art. The specific speed and contrast measurement procedure followed is of little significance, provided each of the blue, green, and red records are identically measured for purposes of comparison. A variety of standard sensitometric

measurement procedures for multicolor photographic elements intended for differing photographic applications have been published by ANSI. The following are representative: American Standard PH2.21-1979, PH2.47-1979, and PH2.27-1979.

The multicolor photographic elements capable of replicating accurately colors when exposed in daylight offer significant advantages over conventional photographic elements exhibiting these characteristics. In the photographic elements the limited blue sensitivity of the green and red spectrally sensitized tabular silver bromoiodide emulsion layers of this invention can be relied upon to separate the blue speed of the blue recording emulsion layer and the blue speed of the minus blue recording emulsion layers. Depending upon the specific application, the use of tabular silver bromoiodide grains in the green and red recording emulsion layers can per se provide a desirably large separation in the blue response of the blue and minus blue recording emulsion layers.

In some applications it may be desirable to increase further blue speed separations of blue and minus blue recording emulsion layers by employing conventional blue speed separation techniques to supplement the blue speed separations obtained by the presence of the high aspect ratio tabular grains. For example, if a photographic element places the fastest green recording emulsion layer nearest the exposing radiation source and the fastest blue recording emulsion layer farthest from the exposing radiation source, the separation of the blue speeds of the blue and green recording emulsion layers, though a full order of magnitude (1.0 log E) different when the emulsions are separately coated and exposed, may be effectively reduced by the layer

order arrangement, since the green recording emulsion layer receives all of the blue light during exposure, but the green recording emulsion layer and other overlying layers may absorb or reflect some of the blue light before it reaches the blue recording emulsion layer. In such circumstances employing a higher proportion of iodide in the blue recording emulsion layer can be relied upon to supplement the tabular grains in increasing the blue speed separation of the blue and minus blue recording emulsion layers. When a blue recording emulsion layer is nearer the exposing radiation source than the minus blue recording emulsion layer, a limited density yellow filter material coated between the blue and minus blue recording emulsion layers can be employed to increase blue and minus blue separation. In no instance, however, is it necessary to make use of any of these conventional speed separation techniques to the extent that they in themselves provide an order of magnitude difference in the blue speed separation or an approximation thereof, as has heretofore been required in the art. However, this is not precluded if exceptionally large blue and minus blue speed separation is desired for a specific application. Thus, the multicolor photographic elements replicate accurately image colors when exposed under balanced lighting conditions while permitting a much wider choice in element construction than has heretofore been possible.

Multicolor photographic elements are often described in terms of color-forming layer units. Most commonly multicolor photographic elements contain three superimposed color-forming layer units each containing at least one silver halide emulsion layer capable of recording exposure to a different third of the spectrum and capable of producing a

complementary subtractive primary dye image. Thus, blue, green, and red recording color-forming layer units are used to produce yellow, magenta, and cyan dye images, respectively. Dye imaging materials need not be present in any color-forming layer unit, but can be entirely supplied from processing solutions. When dye imaging materials are incorporated in the photographic element, they can be located in an emulsion layer or in a layer located to receive oxidized developing or electron transfer agent from an adjacent emulsion layer of the same color-forming layer unit.

To prevent migration of oxidized developing or electron transfer agents between color-forming layer units with resultant color degradation, it is common practice to employ scavengers. The scavengers can be located in the emulsion layers themselves, as taught by U.S. Patent 2,937,086 and/or in interlayers between adjacent color-forming layer units, as illustrated by U.S. Patent 2,336,327.

Although each color-forming layer unit can contain a single emulsion layer, two, three, or more emulsion layers differing in photographic speed are often incorporated in a single color-forming layer unit. Where the desired layer order arrangement does not permit multiple emulsion layers differing in speed to occur in a single color-forming layer unit, it is common practice to provide multiple (usually two or three) blue, green, and/or red recording color-forming layer units in a single photographic element.

At least one green or red recording emulsion layer containing tabular bromoiodide grains as described above is located in the multicolor photographic element to receive an increased proportion of

blue light during imagewise exposure of the photographic element. The increased proportion of blue light reaching the high aspect ratio tabular grain emulsion layer can result from reduced blue light absorption by an overlying yellow filter layer or, preferably, elimination of overlying yellow filter layers entirely. The increased proportion of blue light reaching the high aspect ratio tabular emulsion layer can result also from repositioning the color-forming layer unit in which it is contained nearer to the source of exposing radiation. For example, green and red recording color-forming layer units containing green and red recording high aspect ratio tabular grain emulsions, respectively, can be positioned nearer to the source of exposing radiation than a blue recording color-forming layer unit.

The multicolor photographic elements can take any convenient form consistent with the requirements indicated above. Any of the six possible layer arrangements of Table 27a, p. 211, disclosed by Gorokhovskii, Spectral Studies of the Photographic Process, Focal Press, New York, can be employed. To provide a simple, specific illustration, it is possible to add to a conventional multicolor silver halide photographic element during its preparation one or more high aspect ratio tabular grain emulsion layers sensitized to the minus blue portion of the spectrum and positioned to receive exposing radiation prior to the remaining emulsion layers. However, in most instances it is preferred to substitute one or more minus blue recording high aspect ratio tabular grain emulsion layers for conventional minus blue recording emulsion layers, optionally in combination with layer order arrangement modifications. Alternative layer arrangements can be better appreciated by reference to further preferred illustrative forms.

Layer Order Arrangement I

Exposure

↓

B

IL

TG

IL

TR

Layer Order Arrangement II

Exposure

↓

TFB

IL

TFG

IL

TFR

IL

SB

IL

SG

IL

SR

Layer Order Arrangement III

Exposure

↓

TG

IL

TR

IL

B

Layer Order Arrangement IV

Exposure

↓

TFG

IL

TFR

IL

TSG

IL

TSR

IL

B

Layer Order Arrangement V

Exposure

↓

TFG

IL

TFR

IL

TFB

IL

TSG

IL

TSR

IL

SB

Layer Order Arrangement VI

Exposure

↓

TFR

IL

TB

IL

TFG

IL

TFR

IL

SG

IL

SR

Layer Order Arrangement VII

Exposure

↓

TFR

IL

TFG

IL

TB

IL

TFG

IL

TSG

IL

TFR

IL

TSR

where

B, G, and R designate blue, green, and red recording color-forming layer units, respectively, of any conventional type;

T appearing before the color-forming layer unit B, G, or R indicates that the emulsion layer or layers contain a high aspect ratio tabular grain silver bromoiodide emulsions, as more specifically described above,

F appearing before the color-forming layer unit B, G, or R indicates that the color-forming layer unit is faster in photographic speed than at least one other color-forming layer unit which records light exposure in the same third of the spectrum in the same Layer Order Arrangement;

S appearing before the color-forming layer unit B, G, or R indicates that the color-forming layer unit is slower in photographic speed than at least one other color-forming layer unit which records light exposure in the same third of the spectrum in the same Layer Order Arrangement; and

IL designates an interlayer containing a scavenger, but substantially free of yellow filter material. Each faster or slower color-forming layer unit can differ in photographic speed from another color-forming layer unit which records light exposure in the same third of the spectrum as a result of its position in the Layer Order Arrangement, its inherent speed properties, or a combination of both.

In Layer Order Arrangements I through VII, the location of the support is not shown. Following customary practice, the support will in most instances be positioned farthest from the source of exposing radiation--that is, beneath the layers as shown. If the support is colorless and specularly transmissive--i.e., transparent, it can be located between the exposure source and the indicated layers. Stated more generally, the support can be located between the exposure source and any color-forming layer unit intended to record light to which the support is transparent.

Turning first to Layer Order Arrangement I, it can be seen that the photographic element is free of yellow filter material. However, following conventional practice for elements containing yellow filter material, the blue recording color-forming layer unit lies nearest the source of exposing radiation. In a simple form each color-forming layer unit is comprised of a single silver halide emulsion layer. In another form each color-forming layer unit can contain two, three, or more different silver halide emulsion layers. When a triad of emulsion layers, one of highest speed from each of the color-forming layer units, are compared, they are preferably substantially matched in contrast and the photographic speed of the green and red recording emulsion layers differ from the speed of the blue recording emulsion layer by less than 0.3 log E. When there are two, three, or more different emulsion layers differing in speed in each colorforming layer unit, there are preferably two, three, or more triads of emulsion layers in Layer Order Arrangement I having the stated contrast and speed relationship. The absence of yellow filter material beneath the blue recording color-forming unit increases the photographic speed of this unit.

It is not necessary that the interlayers be substantially free of yellow filter material in Layer Order Arrangement I. Less than conventional amounts of yellow filter material can be located between the blue and green recording color-forming units without departing from the teachings of this invention. Further, the interlayer separating the green and red recording color-forming layer units can contain up to conventional amounts of yellow filter material without departing from the invention. Where conventional amounts of yellow filter material are

employed, the red recording color-forming unit is not restricted to the use of tabular silver bromoiodide grains, as described above, but can take any conventional form, subject to the contrast and speed considerations indicated.

To avoid repetition, only features that distinguish Layer Order Arrangements II through VII from Layer Order Arrangement I are specifically discussed. In Layer Order Arrangement II, rather than incorporate faster and slower blue, red, or green recording emulsion layers in the same color-forming layer unit, two separate blue, green, and red recording color-forming layer units are provided. Only the emulsion layer or layers of the faster color-forming units need contain tabular bromoiodide grains, as described above. The slower green and red recording color-forming layer units because of their slower speeds as well as the overlying faster blue recording color-forming layer unit, are adequately protected from blue light exposure without employing a yellow filter material. The use of high aspect ratio tabular grain silver bromoiodide emulsions in the emulsion layer or layers of the slower green and/or red recording color-forming layer units is, of course, not precluded. In placing the faster red recording color-forming layer unit above the slower green recording color-forming layer unit, increased speed can be realized, as taught by U.S. Patent 4,184,876, and German OLS 2,704,797; 2,622,923; 2,622,924; and 2,704,826.

Layer Order Arrangement III differs from Layer Order Arrangement I in placing the blue recording color-forming layer unit farthest from the exposure source. This then places the green recording color-forming layer unit nearest and the red recording color-forming layer unit nearer the

exposure source. This arrangement is highly advantageous in producing sharp, high quality multicolor images. The green recording color-forming layer unit, which makes the most important visual contribution to multicolor imaging, as a result of being located nearest the exposure source is capable of producing a very sharp image, since there are no overlying layers to scatter light. The red recording color-forming layer unit, which makes the next most important visual contribution to the multicolor image, receives light that has passed through only the green recording color-forming layer unit and has therefore not been scattered in a blue recording color-forming layer unit. Though the blue recording color-forming layer unit suffers in comparison to Layer Order Arrangement I, the loss of sharpness does not offset the advantages realized in the green and red recording color-forming layer units, since the blue recording color-forming layer unit makes by far the least significant visual contribution to the multicolor image produced.

Layer Order Arrangement IV expands Layer Order Arrangement III to include green and red recording color-forming layer units containing separate faster and slower high aspect ratio tabular grain emulsion. Layer Order Arrangement V differs from Layer Order Arrangement IV in providing an additional blue recording color-forming layer unit above the slower green, red, and blue recording color- forming layer units. The faster blue recording color-forming layer unit employs high aspect ratio tabular grain silver bromoiodide emulsion, as described above. The faster blue recording color- forming layer unit in this instance acts to absorb blue light and therefore reduces the proportion of blue light reaching the slower green

and red recording color-forming layer units. In a variant form, the slower green and red recording color-forming layer units need not employ high aspect ratio tabular grain emulsions.

Layer Order Arrangement VI differs from Layer Order Arrangment IV in locating a tabular grain blue recording color-forming layer unit between the green and red recording color-forming layer units and the source of exposing radiation. As is pointed out above, the tabular grain blue recording color-forming layer unit can be comprised of one or more tabular grain blue recording emulsion layers and, where multiple blue recording emulsion layers are present, they can differ in speed. To compensate for the less favored position which the red recording color-forming layer units would otherwise occupy, Layer Order Arrangement VI also differs from Layer Order Arrangement IV in providing a second fast red recording color-forming layer unit, which is positioned between the tabular grain blue recording color- forming layer unit and the source of exposing radiation. Because of the favored location which the second tabular grain fast red recording colorforming layer unit occupies it is faster than the first fast red recording layer unit if the two fast redrecording layer units incorporate identical emulsions. It is, of course, recognized that the first and second fast tabular grain red recording color- forming layer units can, if desired, be formed of the same or different emulsions and that their relative speeds can be adjusted by techniques well known to those skilled in the art. Instead of employing two fast red recording layer units, as shown, the second fast red recording layer unit can, if desired, be replaced with a second fast green recording color- forming layer unit. Layer Order Arrangement VII can be

identical to Layer Order Arrangement VI, but differs in providing both a second fast tabular grain red recording color-forming layer unit and a second fast tabular grain green recording color-forming layer unit interposed between the exposing radiation source and the tabular grain blue recording color- forming layer unit.

There are, of course, many other advantageous layer order arrangements possible, Layer Order Arrangements I through VII being merely illustrative. In each of the various Layer Order Arrangements corresponding green and red recording color- forming layer units can be interchanged--i.e., the faster red and green recording color-forming layer units can be interchanged in position in the various layer order arrangements and additionally or alternatively the slower green and red recording color- forming layer units can be interchanged in position.

Although photographic emulsions intended to form multicolor images comprised of combinations of subtractive primary dyes normally take the form of a plurality of superimposed layers containing incorporated dye-forming materials, such as dye-forming couplers, this is by no means required. Three color-forming components, normally referred to as packets, each containing a silver halide emulsion for recording light in one third of the visible spectrum and a coupler capable of forming a complementary subtractive primary dye, can be placed together in a single layer of a photographic element to produce multicolor images. Exemplary mixed packet multicolor photographic elements are disclosed by U.S. Patents 2,698,794 and 2,843,489.

It is the relatively large separation in the blue and minus blue sensitivities of the green and

red recording color-forming layer units containing tabular grain silver bromoiodide emulsions that permits reduction or elimination of yellow filter materials and/or the employment of novel layer order arrangements. One technique that can be employed for providing a quantitative measure of the relative response of green and red recording color-forming layer units to blue light in multicolor photographic elements is to expose through a step tablet a sample of a multicolor photographic element according to this invention employing first a neutral exposure source--i.e., light at 5500°K--and thereafter to process the sample. A second sample is then identically exposed, except for the interposition of a Wratten 98 filter, which transmits only light between 400 and 490 nm, and thereafter identically processed. Using blue, green, and red transmission densities determined according to American Standard PH2.1-1952, as described above, three dye characteristic curves can be plotted for each sample. The differences Δ and Δ' in blue speed of the blue recording color-forming layer unit(s) and the blue speed of the green or red recording color-forming layer unit(s) can be determined from the relationship:

(A) $\Delta = (B_{W98} - G_{W98}) - (B_N - G_N)$ or

(B) $\Delta' = (B_{W98} - R_{W98}) - (B_N - R_N)$

where

B_{W98} is the blue speed of the blue recording color-forming layer unit(s) exposed through the Wratten 98 filter;

G_{W98} is the blue speed of the green recording color-forming layer unit(s) exposed through the Wratten 98 filter;

R_{W98} is the blue speed of the red recording color-forming layer unit(s) exposed through the Wratten 98 filter;

B_N is the blue speed of the blue recording color-forming layer unit(s) exposed to neutral (5500°K) light;

G_N is the green speed of the green recording color-forming layer unit(s) exposed to neutral (5500°K) light; and

R_N is the red speed of the red recording color-forming layer unit(s) exposed to neutral (5500°K) light.

The above description imputes blue, green, and red densities to the blue, green, and red recording color-forming layer units, respectively, ignoring unwanted spectral absorption by the yellow, magenta, and cyan dyes. Such unwanted spectral absorption is rarely of sufficient magnitude to affect materially the results obtained for the purposes they are here employed.

The multicolor photographic elements in the absence of any yellow filter material exhibit a blue speed by the blue recording color-forming layer units which is at least 6 times, preferably at least 8 times, and optimally at least 10 times the blue speed of green and/or red recording color-forming layer units containing high aspect ratio tabular grain emulsions, as described above. By way of comparison, an example below demonstrates that a conventional multicolor photographic element lacking yellow filter material exhibits a blue speed difference between the blue recording color-forming layer unit and the green recording color-forming layer unit(s) of less than 4 times (0.55 log E) as compared to nearly 10 times (0.95 log E) for a comparable multicolor photographic element according to the present invention. This comparison illustrates the advantageous reduction in blue speed of green recording color-forming layer units that can be achieved using high aspect ratio tabular grain silver bromoiodide emulsions.

Another measure of the large separation in the blue and minus blue sensitivities of multicolor photographic elements is to compare the green speed of a green recording color-forming layer unit or the red speed of a red recording color-forming layer unit to its blue speed. The same exposure and processing techniques described above are employed, except that the neutral light exposure is changed to a minus blue exposure by interposing a Wratten 9 filter, which transmits only light beyond 490 nm. The quantitative differences Δ'' and Δ''' being determined are

(C) $\Delta'' = G_{W9} - G_{W98}$ or

(D) $\Delta''' = R_{W9} - R_{W98}$

where

G_{W98} and R_{W98} are defined above;

G_{W9} is the green speed of the green recording color-forming layer unit(s) exposed through the Wratten 9 filter; and

R_{W9} is the red speed of the red recording color-forming layer unit(s) exposed through the Wratten 9 filter. Again unwanted spectral absorption by the dyes is rarely material and is ignored.

Red and green recording color-forming layer units containing tabular silver bromoiodide emulsions, as described above, exhibit a difference between their speed in the blue region of the spectrum and their speed in the portion of the spectrum to which they are spectrally sensitized (i.e., a difference in their blue and minus blue speeds) of at least 10 times (1.0 log E), preferably at least 20 times (1.3 log E). In an example below the difference is greater than 20 times (1.35 log E) while for the comparable conventional multicolor photographic element lacking yellow filter material this difference is less than 10 times (0.95 log E).

In comparing the quantitative relationships A to B and C to D for the same element, the results will not be identical, even if the green and red recording color-forming layer units are identical (except for their wavelengths of spectral sensitization). The reason is that in most instances the red recording color-forming layer unit(s) will be receiving light that has already passed through the corresponding green recording color-forming layer unit(s). However, if a second element is prepared which is identical to the first, except that the corresponding green and red recording color-forming layer units have been interchanged in position, then the red recording color-forming layer unit(s) of the second element should exhibit substantially identical values for relationships B and D that the green recording color-forming layer units of the first element exhibit for relationships A and C, respectively. Stated more succinctly, the mere choice of green spectral sensitization as opposed to red spectral sensitization does not significantly influence the values obtained by the above quantitative comparisons. Therefore, it is common practice not to differentiate green and red speeds in comparision to blue speed, but to refer to green and red speeds generically as minus blue speeds.

The high aspect ratio tabular grain silver bromoiodide emulsions of the present invention are advantageous because of their reduced high angle light scattering as compared to nontabular and lower aspect ratio tabular grain emulsions. This can be quantitatively demonstrated. Referring to Figure 5, a sample of an emulsion 1 according to the present invention is coated on a transparent (specularly transmissive) support 3 at a silver coverage of 1.08 g/m^2. Although not shown, the emulsion and support

are preferably immersed in a liquid having a substantially matched refractive index to minimize Fresnel reflections at the surfaces of the support and the emulsion. The emulsion coating is exposed perpendicular to the support plane by a collimated light source 5. Light from the source following a path indicated by the dashed line 7, which forms an optical axis, strikes the emulsion coating at point A. Light which passes through the support and emulsion can be sensed at a constant distance from the emulsion at a hemispherical detection surface 9. At a point B, which lies at the intersection of the extension of the initial light path and the detection surface, light of a maximum intensity level is detected.

An arbitrarily selected point C is shown in Figure 5 on the detection surface. The dashed line between A and C forms an angle ϕ with the emulsion coating. By moving point C on the detection surface it is possible to vary ϕ from 0 to 90°. By measuring the intensity of the light scattered as a function of the angle ϕ it is possible (because of the rotational symmetry of light scattering about the optical axis 7) to determine the cumulative light distribution as a function of the angle ϕ. For a background description of the cumulative light distribution see DePalma and Gasper, "Determining the Optical Properties of Photographic Emulsions by the Monte Carlo Method", Photographic Science and Engineering, Vol. 16, No. 3, May-June 1971, pp. 181-191.

After determining the cumulative light distribution as a function of the angle ϕ at values from 0 to 90° for the emulsion 1 according to the present invention, the same procedure is repeated, but with a conventional emulsion of the same average

grain volume coated at the same silver coverage on another portion of support 3. In comparing the cumulative light distribution as a functon of the angle ϕ for the two emulsions, for values of ϕ up to 70° (and in some instances up to 80° and higher) the amount of scattered light is lower with the emulsions according to the present invention. In Figure 5 the angle θ is shown as the complement of the angle ϕ. The angle of scattering is herein discussed by reference to the angle θ. Thus, the high aspect ratio tabular grain emulsions of this invention exhibit less high-angle scattering. Since it is high-angle scattering of light that contributes disproportionately to reduction in image sharpness, it follows that the high aspect ratio tabular grain emulsions of the present invention are in each instance capable of producing sharper images.

As herein used the term "collection angle" is the value of the angle θ at which half of the light striking the detection surface lies within an area subtended by a cone formed by rotation of line AC about the polar axis at the angle θ while half of the light striking the detection surface strikes the detection surface within the remaining area.

While not wishing to be bound by any particular theory to account for the reduced high angle scattering properties of high aspect ratio tabular grain emulsions according to the present invention, it is believed that the large flat major crystal faces presented by the high aspect ratio tabular grains as well as the orientation of the grains in the coating account for the improvements in sharpness observed. Specifically, it has been observed that the tabular grains present in a silver halide emulsion coating are substantially aligned with the planar support surface on which they lie.

Thus, light directed perpendicular to the photographic element striking the emulsion layer tends to strike the tabular grains substantially perpendicular to one major crystal face. The thinness of tabular grains as well as their orientation when coated permits the high aspect ratio tabular grain emulsion layers of this invention to be substantially thinner than conventional emulsion coatings, which can also contribute to sharpness. However, the emulsion layers of this invention exhibit enhanced sharpness even when they are coated to the same thicknesses as conventional emulsion layers.

In a specific preferred form of the invention the high aspect ratio tabular grains exhibit a minimum average grain diameter of at least 1.0 micrometer, most preferably at least 2 micrometers. Both improved speed and sharpness are attainable as average grain diameters are increased. While maximum useful average grain diameters will vary with the graininess that can be tolerated for a specific imaging application, the maximum average grain diameters of high aspect ratio tabular grain emulsions according to the present invention are in all instances less than 30 micrometers, preferably less than 15 micrometers, and optimally no greater than 10 micrometers.

In addition to producing the sharpness advantages indicated above at the average diameters indicated it is also noted that the high aspect ratio tabular grain emulsions avoid a number of disadvantages encountered by conventional emulsions having these large average grain diameters. First, it is difficult to prepare conventional, nontabular emulsions with average grain diameters above 2 micrometers. Second, Farnell in "The Relationship Between Speed and Grain Size", The Journal of Photographic Science, 17, 1969, pp. 116-125, pointed to reduced

speed performance at average grain diameters above 0.8 micrometer. Further, in employing conventional emulsions of high average grain diameters a much larger volume of silver is present in each grain as compared to tabular grains of comparable diameter. Thus, unless conventional emulsions are coated at higher silver coverages, which, of course, is a very real practical disadvantage, the graininess produced by the conventional emulsions of large average grain diameters is higher than with the emulsions of this invention having the same average grain diameters. Still further, if large grain diameter conventional emulsions are employed, with or without increased silver coverages, then thicker coatings are required to accommodate the corresponding large thicknesses of the larger diameter grains. However, tabular grain thicknesses can remain very low even while diameters are above the levels indicated to obtain sharpness advantages. Finally, the sharpness advantages produced by tabular grains are in part a distinct function of the shape of the grains as distinguished from merely their average diameters and therefore capable of rendering sharpness advantages over conventional nontabular grains.

Although it is possible to obtain reduced high angle scattering with single layer coatings of high aspect ratio tabular grain emulsions according to the present invention, it does not follow that reduced high angle scattering is necessarily realized in multicolor coatings. In certain multicolor coating formats enhanced sharpness can be achieved with the high aspect ratio tabular grain emulsions of this invention, but in other multicolor coating formats the high aspect ratio tabular grain emulsions of this invention can actually degrade the sharpness of underlying emulsion layers.

Referring back to Layer Order Arrangement I, it can be seen that the blue recording emulsion layer lies nearest to the exposing radiation source while the underlying green recording emulsion layer is a tabular grain emulsion according to this invention. The green recording emulsion layer in turn overlies the red recording emulsion layer. If the blue recording emulsion layer contains grains having an average diameter in the range of from 0.2 to 0.6 micrometer, as is typical of many nontabular emulsions, it will exhibit maximum scattering of light passing through it to reach the green and red recording emulsion layers. Unfortunately, if light has already been scattered before it reaches the high aspect ratio tabular grain emulsion forming the green recording emulsion layer, the tabular grains can scatter the light passing through to the red recording emulsion layer to an even greater degree than a conventional emulsion. Thus, this particular choice of emulsions and layer arrangement results in the sharpness of the red recording emulsion layer being significantly degraded to an extent greater than would be the case if no emulsions according to this invention were present in the layer order arrangement.

In order to realize fully the sharpness advantages in an emulsion layer that underlies a high aspect ratio tabular grain silver bromoiodide emulsion layer according to the present invention it is preferred that the tabular grain emulsion layer be positioned to receive light that is free of significant scattering (preferably positioned to receive substantially specularly transmitted light). Stated another way, improvements in sharpness in emulsion layers underlying tabular grain emulsion layers are best realized only when the tabular grain emulsion

layer does not itself underlie a turbid layer. For example, if a high aspect ratio tabular grain green recording emulsion layer overlies a red recording emulsion layer and underlies a Lippmann emulsion layer and/or a high aspect ratio tabular grain blue recording emulsion layer according to this invention, the sharpness of the red recording emulsion layer will be improved by the presence of the overlying tabular grain emulsion layer or layers. Stated in quantitative terms, if the collection angle of the layer or layers overlying the high aspect ratio tabular grain green recording emulsion layer is less than about 10°, an improvement in the sharpness of the red recording emulsion layer can be realized. It is, of course, immaterial whether the red recording emulsion layer is itself a high aspect ratio tabular grain emulsion layer according to this invention insofar as the effect of the overlying layers on its sharpness is concerned.

In a multicolor photographic element containing superimposed color-forming units it is preferred that at least the emulsion layer lying nearest the source of exposing radiation be a high aspect ratio tabular grain emulsion in order to obtain the advantages of sharpness. In a specifically preferred form each emulsion layer which lies nearer the exposing radiation source than another image recording emulsion layer is a high aspect ratio tabular grain emulsion layer. Layer Order Arrangements II, III, IV, V, VI, and VII, described above, are illustrative of multicolor photographic element layer arrangements which are capable of imparting significant increases in sharpness to underlying emulsion layers.

Although the advantageous contribution of high aspect ratio tabular grain silver bromoiodide emulsions to image sharpness in multicolor photographic elements has been specifically described by

reference to multicolor photographic elements, sharpness advantages can also be realized in multilayer black-and-white photographic elements intended to produce silver images. It is conventional practice to divide emulsions forming black-and-white images into faster and slower layers. By employing high aspect ratio tabular grain emulsions according to this invention in layers nearest the exposing radiation source the sharpness of underlying emulsion layers will be improved.

Further applications filed concurrently with the present one describe in further detail subject matter which is referred to above. The U.K. specification numbers are 2,110,831, 2,110,404, 2,110,405, 2,112,157, 2,110,402, 2,109,577, 2,110,830, 2,110,403, 2,111,706, 2,109,578 and 2,111,231.

The invention is further illustrated by the following specific examples:

In each of the examples the contents of the reaction vessel were stirred vigorously throughout silver and halide salt introductions; the term "percent" means percent by weight, unless otherwise indicated; and the term "M" stands for a molar concentration, unless otherwise indicated. All solutions, unless otherwise indicated, are aqueous solutions.

Example 1

To 4.55 liters of a 2.4 percent phthalated (see U.S. Patents 2,614,928 and 2,614,929) gelatin solution at 71°C, pH 5.8, adjusted to a pBr of 1.3 with potassium bromide, were added with stirring and by double-jet a 1.40 M solution of potassium bromide which was also 0.088 M in potassium iodide, and a 1.46 M solution of silver nitrate over a period of 27 minutes, while maintaining the pBr at 1.3. Approximately 4.6 moles of silver nitrate was consumed. The emulsion was cooled to 50°C and held for 15 minutes in the presence of 8.9 g/mole Ag sodium thiocyanate.

The emulsion was then coagulation washed by the method of U.S. Patent 2,614,928. In each of the samples under this and subsequent headings the contents of the reaction vessel were stirred vigorously throughout silver and halide salt introductions.

A photomicrograph of the emulsion prepared is shown in Figure 1. The average diameter of the tabular grains was 1.25 micrometers and their average thickness 0.07 micrometer. The average aspect ratio of the tabular grains was 18:1. The tabular grains accounted for 72 percent of the total projected area of the silver halide grains. The silver halide grains precipitated consisted of silver bromoiodide (6 mole percent iodide).

Example 2

To 22 liters of a 2.27 percent phthalated gelatin solution at 70°C containing 0.060 M sodium bromide were added with stirring and by double-jet with equal constant flow rates, a 0.97 M sodium bromide solution which was also 0.027 M in potassium iodide and a 1.0 M silver nitrate solution over a 30 second period while maintaining a pBr of 1.2 (consuming 1.6 percent of the total silver nitrate used). The twin jet addition was continued for an additional 5.5 minutes, maintaining a pBr of 1.2 and at a rate consuming 4.5 percent of the total silver nitrate used. Addition was halted, and then a 3.88 M sodium bromide solution which was also 0.12 M in sodium iodide and a 4.0 M silver nitrate solution were added concurrently over a period of 9.5 minutes maintaining pBr 1.2 at an accelerated flow rate (4.8X from start to finish, i.e. 4.8 times faster at the end than at the start) consuming 90.8 percent of the total silver used. A 0.40 M silver nitrate solution was then added until a pBr of 3.4 was attained (consuming approximately 3 percent of the total silver nitrate used). A total of approximately 37 moles of silver nitrate was used.

The emulsion was then coagulation washed similarly to Example 1.

Electron micrographs showed that this emulsion was comprised of tabular silver bromoiodide grains (3 mole percent iodide) having an average grain diameter of 0.94 μm, and an average thickness of approximately 0.07 μm. The tabular silver bromoiodide grains exhibited an average aspect ratio of 13:1 and accounted for 73 percent of the total projected area. Figure 2 is a photomicrograph of a sample of the emulsion prepared by this example.

Examples to Illustrate Speed/Granularity Relationships

A series of silver bromoiodide emulsions of varying aspect ratio were prepared as described below. The physical descriptions of the emulsions are given in Table I following the preparation of Emulsion No. 7.

A. Emulsion Preparation and Sensitization

Emulsion 1 (Example)

To 5.5 liters of a 1.5 percent gelatin, 0.17 M potassium bromide solution at 80°C, were added with stirring and by double-jet, 2.2 M potassium bromide and 2.0 M silver nitrate solutions over a two minute period, while maintaining a pBr of 0.8 (consuming 0.56 percent of the total silver nitrate used). The bromide solution was stopped and the silver nitrate solution continued for 3 minutes (consuming 5.52 percent of the total silver nitrate used). The bromide and silver nitrate solutions were then run concurrently maintaining pBr 1.0 in an accelerated flow (2.2X from start to finish) over 13 minutes (consuming 34.8 percent of the total silver nitrate used). The bromide solution was stopped and the silver nitrate solution run for 1.7 minutes (consuming 6.44 percent of the total silver nitrate used). A 1.8 M potassium bromide solution which was

also 0.24 M in potassium iodide was added with the silver nitrate solution for 15.5 minutes by double-jet in an accelerated flow (1.6X from start to finish), consuming 45.9 percent of the total silver used, maintaining a pBr of 1.6. Both solutions were stopped and a 5 minute digest using 1.5 g sodium thiocyanate/mole Ag was carried out. A 0.18 M potassium iodide solution and the silver nitrate solution were double-jetted at equal flow rates until a pBr of 2.9 was reached (consuming 6.8 percent of the total silver nitrate used). A total of approximately 11 moles of silver nitrate was used. The emulsion was cooled to 30°C, and washed by the coagulation method of U.S. Patent 2,614,929. To the emulsion at 40°C were added 464 mg/mole Ag of the green spectral sensitizer, anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)- 3-(3-sulfopropyl)-oxacarbocyanine hydroxide, sodium salt, and the pAg adjusted to 8.4 after a 20 minute hold. To the emulsion was added 3.5 mg/mole Ag of sodium thiosulfate pentahydrate and 1.5 mg/mole Ag of potassium tetrachloroaurate. The pAg was adjusted to 8.1 and the emulsion was then heated for 5 minutes at 65°C.

Emulsion 2 (Example)

To 5.5 liters of a 1.5 percent gelatin, 0.17 M potassium bromide solution at 80°C, pH 5.9, were added with stirring and by double-jet 2.1 M potassium bromide and 2.0 M silver nitrate solutions over a two minute period while maintaining a pBr of 0.8 (consuming 0.53 percent of the total silver nitrate used). The bromide solution was stopped and the silver nitrate solution continued for 4.6 minutes at a rate consuming 8.6 percent of the total silver nitrate used. The bromide and silver nitrate solutions were then run concurrently for 13.3 minutes, maintaining a pBr of 1.2 in an accelerated

flow (2.5X from start to finish), consuming 43.6 percent of the total silver nitrate used. The bromide solution was stopped and the silver nitrate solution run for one minute (consuming 4.7 percent of the total silver nitrate used).

A 2.0 M potassium bromide solution which was also 0.30 M in potassium iodide was double-jetted with the silver nitrate solution for 13.3 minutes in an accelerated flow (1.5X from start to finish), maintaining a pBr of 1.7, and consuming 35.9 percent of the total silver nitrate used. To the emulsion was added 1.5 g/mole Ag of sodium thiocyanate and the emulsion was held for 25 minutes. A 0.35 M potassium iodide solution and the silver nitrate solution were double-jetted at a constant equal flow rate for approximately 5 minutes until a pBr of 3.0 was reached (consuming approximately 6.6 percent of the total silver nitrate used). The total silver nitrate consumed was approximately 11 moles. A solution of 350 g of phthalated gelatin in 1.2 liters of water was then added, the emulsion cooled to 30°C, and washed by the coagulation method of Emulsion 1. The emulsion was then optimally spectrally and chemically sensitized in a manner similar to that described for Emulsion 1.

Emulsion 3 (Example)

To 30.0 liters of a 0.8 percent gelatin, 0.10 M potassium bromide solution at 75°C were added with stirring and by double-jet, 1.2 M potassium bromide and 1.2 M silver nitrate solution over a 5 minute period while maintaining a pBr of 1.0 (consuming 2.1 percent of the total silver nitrate used). A 5.0 liter solution containing 17.6 percent phthalated gelatin was then added, and the emulsion held for one minute. The silver nitrate solution was then run into the emulsion until a pBr of 1.35 was

attained, consuming 5.24 percent of the total silver nitrate used. A 1.06 M potassium bromide solution which was also 0.14 M in potassium iodide was double-jetted with the silver nitrate solution in an accelerated flow (2X from start to finish) consuming 92.7 percent of the total silver nitrate used, and maintaining pBr 1.35. A total of approximately 20 moles of silver nitrate was used. The emulsion was cooled to 35°C, coagulation washed, and optimally spectrally and chemically sensitized in a manner similar to that described for Emulsion 1.

Emulsion 4 (Example)

To 4.5 liters of a 1.5 percent gelatin, 0.17 M potassium bromide solution at 55°C, pH 5.6, were added with stirring and by double-jet, 1.8 M potassium bromide and 2.0 M silver nitrate solutions at a constant equal rate over a period of one minute at a pBr of 0.8 (consuming 0.7 percent of the total silver nitrate used). The bromide, silver, and a 0.26 M potassium iodide solution were then run concurrently at an equal constant rate over 7 minutes, maintaining pBr 0.8, and consuming 4.8 percent of the total silver nitrate used. The triple run was then continued over an additional period of 37 minutes maintaining pBr 0.8 in an accelerated flow (4X from start to finish), consuming 94.5 percent of the total silver nitrate used. A total of approximately 5 moles silver nitrate was used. The emulsion was cooled to 35°C, 1.0 liter of water containing 200 g of phthalated gelatin was added, and the emulsion was coagulation washed. The emulsion was then optimally spectrally and chemically sensitized in a manner similar to that described for Emulsion 1.

Emulsion 5 (Control)--This emulsion was precipitated in the manner described in U.S. Patent 4,184,877.

To a 5 percent solution of gelatin in 17.5 liters of water at 65°C were added with stirring and by double-jet 4.7 M ammonium iodide and 4.7 M silver nitrate solutions at a constant equal flow rate over a 3 minute period while maintaining a pI of 2.1 (consuming approximately 22 percent of the silver used in the seed grain preparation). The flow of both solutions was then adjusted to a rate consuming approximately 78 percent of the total silver nitrate used in the seed grain preparation over a period of 15 minutes. The run of the ammonium iodide solution was then stopped, and the addition of the silver nitrate solution continued to a pI of 5.0. A total of approximately 56 moles of silver nitrate was used in the preparation of the seed grain emulsion. The emulsion was cooled to 30°C and used as a seed grain emulsion for further precipitation as described hereinafter. The average diameter of the seed grains was 0.24 micrometer.

15.0 liter of a 5 percent gelatin solution containing 4.1 moles of the AgI emulsion as prepared above was heated to 65°C. A 4.7 M ammonium bromide solution and a 4.7 M silver nitrate solution were added by double-jet at an equal constant flow rate over a period of 7.1 minutes while maintaining a pBr of 4.7 (consuming 40.2 percent of the total silver nitrate used in the precipitation on the seed grains). Addition of the ammonium bromide solution alone was then continued until a pBr of approximately 0.9 was attained at which time it was stopped. 2.7 liter of a solution of 11.7 M ammonium hydroxide was then added, and the emulsion was held for 10 minutes. The pH was adjusted to 5.0 with sulfuric acid, and the double-jet introduction of the ammonium bromide and silver nitrate solution was resumed for 14 minutes maintaining a pBr of approximately 0.9 and

at a rate consuming 56.8 percent of the total silver nitrate consumed. The pBr was then adjusted to 3.3 and the emulsion cooled to 30°C. A total of approximately 87 moles of silver nitrate was used. 900 g of phthalated gelatin were added, and the emulsion was coagulation washed.

The pAg of the emulsion was adjusted to 8.8 and to the emulsion was added 4.2 mg/mole Ag of sodium thiosulfate pentahydrate and 0.6 mg/mole Ag of potassium tetrachloroaurate. The emulsion was then heat finished for 16 minutes at 80°C, cooled to 40°C, 387 mg/mole Ag of the green spectral sensitizer, anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt, was added and the emulsion was held for 10 minutes. Chemical and spectral sensitization was optimum for the sensitizers employed.

Emulsion No. 6 (Control)--This emulsion is of the type described in U.S. Patent 3,320,069.

To 42.0 liters of a 0.050 M potassium bromide, 0.012 M potassium iodide and 0.051 M potassium thiocyanate solution at 68°C containing 1.25 percent phthalated gelatin were added by double-jet with stirring at equal flow rates a 1.32 M potassium bromide solution which was also 0.11 M in potassium iodide and a 1.43 M silver nitrate solution, over a period of approximately 40 minutes. The precipitation consumed 21 moles of silver nitrate. The emulsion was then cooled to 35°C and coagulation washed by the method of U.S. Patent 2,614,928.

The pAg of the emulsion was adjusted to 8.1 and to the emulsion was added 5.0 mg/mole Ag of sodium thiosulfate pentahydrate and 2.0 mg/mole Ag of potassium tetrachloroaurate. The emulsion was then heat finished at 65°C, cooled to 40°C, and 464

mg/mole Ag of the green spectral sensitizer, anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)-oxacarbocyanine hydroxide, sodium salt, was added and the emulsion was held for 10 minutes. Chemical and spectral sensitization was optimum for the sensitizers employed.

Emulsion No. 7 (Control)--This emulsion is of the type described in U.S. Patent 3,320,069.

To 42.0 liters of a 0.050 M potassium bromide, 0.012 M potassium iodide, and 0.051 M potassium thiocyanate solution at 68°C containing 1.25 percent phthalated gelatin were added by double-jet with stirring at equal flow rates a 1.37 M potassium bromide solution which was also 0.053 M in potassium iodide, and a 1.43 M silver nitrate solution, over a period of approximately 40 minutes. The precipitation consumed 21 moles of silver nitrate. The emulsion was then cooled to 35°C and coagulation washed in the same manner as Emulsion 6.

The pAg of the emulsion was adjusted to 8.8 and to the emulsion was added 10 mg/mole Ag of sodium thiosulfate pentahydrate and 2.0 mg/mole Ag of potassium tetrachloroaurate. The emulsion was then heat finished at 55°C, cooled to 40°C, 387 mg/mole Ag of the green spectral sensitizer, anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)-oxacarbocyanine hydroxide, sodium salt, was added and the emulsion was held for 10 minutes. Chemical and spectral sensitization was optimum for the sensitizers employed.

TABLE I

PHYSICAL DESCRIPTIONS OF EMULSION 1-7

	Emulsion No.	Iodide Content (M%I)	Tabular Grain Diameter (μm)	Tabular Grain Thickness (μm)	Average Aspect Ratio	% of Projected Area
Example	1	6	≈3.8	0.14	27:1	>50
Example	2	1.2	≈3.8	0.14	27:1	75
Example	3	12.0	2.8	0.15	19:1	>90
Example	4	12.3	1.8	0.12	15:1	>50
Control	5	4.7	1.4	0.42	3.3:1	--
Control	6	10	1.1	≈0.40	2.8:1*	--
Control	7	5	1.0	≈0.40	2.5:1*	--

* U.S. Patent 3,320,069 does not disclose aspect ratios. The aspect ratios were determined by repeating the prior art examples and measuring the grains.

Emulsions 1 through 4 were high aspect ratio tabular grain emulsions within the preferred definition limits of this patent application in that their thickness was less than 0.3 micrometer. Although some tabular grains of less than 0.6 micrometer in diameter were included in computing the tabular grain average diameters and percent projected area in these and subsequent example emulsions, except where this exclusion is specifically noted, insufficient small diameter grains were present to alter significantly the numbers reported. To obtain a representative average aspect ratio for the grains of the control emulsions the average grain diameter was compared to the average grain thickness. Although not measured, the projected area that could be attributed to the few tabular grains meeting the less than 0.3 micrometer thickness and at least 0.6 micrometer diameter criteria was in each

instance estimated by visual inspection. This projected area accounted for very little, if any, of the total projected area of the total grain population of the control emulsions.

B. Speed/Granularity of Single Layer Incorporated Coupler Photographic Materials

The chemically and spectrally sensitized emulsions (Emulsion Nos. 1-7) were separately coated in a single-layer magenta format on a cellulose triacetate film support. Each coated element comprised a silver halide emulsion at 1.07 g silver/m^2, gelatin at 2.14 g/m^2, a solvent dispersion of the magenta image-forming coupler 1-(2,4-dimethyl-6-chlorophenyl)-3-[α-(3-n-pentadecylphenoxy)-butyramido]-5-pyrazolone at 0.75 g coupler/m^2, the antistain agent 5-secoctadecyl-hydroquinone-2-sulfonate, potassium salt at 3.2 g/mole Ag, and the antifoggant 4-hydroxy-6- methyl-1,3,3a,7-tetraazaindene at 3.6 g/mole Ag. An overcoat layer, comprising gelatin at 0.88 g/m^2 and the hardener bis(vinylsulfonylmethyl)ether at 1.75 percent based on total gelatin weight of all layers, was applied.

The resulting photographic elements were exposed for 1/100 of a second through a 0-3.0 density step tablet plus a Wratten No. 9 filter and 1.26 density neutral filter, to a 600W, 3000°K tungsten light source. Processing was accomplished at 37.7°C in a color process of the type described in the British Journal of Photography Annual, 1979, pp. 204-206. The development times were varied to produce fog densities of about 0.10. The relative green sensitivity and the rms granularity were determined for each of the photographic elements. (The rms granularity is measured by the method described by H. C. Schmitt, Jr. and J. H. Altman, Applied Optics, 9, pp. 871-874, April 1970.)

The speed-granularity relationship for these coatings is conveniently shown on a plot of Log Green

Speed vs. rms Granularity X 10 in Figure 3. It is clearly shown in Figure 3 that optimally chemically and spectrally sensitized silver bromoiodide emulsions having high aspect ratios exhibit a much better speed-granularity relationship than do the low aspect ratio silver bromoiodide emulsions 5, 6, and 7.

It should be noted that the use of a single-layer format, where all the silver halide emulsions are coated at equal silver coverage and with a common silver/coupler ratio, is the best format to illustrate the speed-granularity relationship of a silver halide emulsion without introducing complicating interactions.

C. Speed/Granularity Improvement in a Multilayer Incorporated Coupler Photographic Element

A multicolor, incorporated coupler photographic element was prepared by coating the following layers on a cellulose triacetate film support in the order recited:

Layer 1 Slow Cyan Layer -- comprising a red sensitized silver bromoiodide grains, gelatin, cyan image-forming coupler, colored coupler, and DIR coupler.

Layer 2 Fast Cyan Layer -- comprising a faster redsensitized silver bromoiodide grains, gelatin, cyan image-forming coupler, colored coupler, and DIR coupler.

Layer 3 Interlayer -- comprising gelatin and 2,5-di-sec-dodecylhydroquinone antistain agent.

Layer 4 Slow Magenta Layer -- comprising a green-sensitized silver bromoiodide grains (1.48 g silver/m^2), gelatin (1.21 g/m^2), the magenta coupler 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-diamylphenoxyacetamido)-benzamido]-5

-pyrazolone (0.88 g/m^2), the colored coupler 1-(2,4,6-trichlorophenyl)-3-[α-(3-tert-butyl-4-hydroxyphenoxy)tetradecanamido-2-chloroanilino]-4-(3,4-dimethoxy)-phenylazo-5-pyrazolone (0.10 g/m^2), the DIR coupler 1-{4-[α-(2,4-di-tert-amylphenoxy)butyramido]phenyl}-3-pyrrolidino4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone (0.02 g/m^2) and the antistain agent 5-sec-octadecylhydroquinone-2-sulfonate, potassium salt (0.09 g/m^2).

Layer 5 Fast Magenta Layer -- comprising a faster green-sensitized silver bromoiodide grains (1.23 g silver/m^2), gelatin (0.88 g/m^2), the magenta coupler 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-diamylphenoxyacetamido)-benzamido]-5-pyrazolone (0.12 g/m^2), the colored coupler 1-(2,4,6-trichlorophenyl)-3-[α-(3-tert-butyl-4-hydroxyphenoxy)tetradecanamido-2-chloroanilino]-4-(3,4-dimethoxy)-phenylazo-5-pyrazolone (0.03 g/m^2), and the antistain agent 5-sec-octadecylhydroquinone 2-sulfonate, potassium salt (0.05 g/m^2).

Layer 6 Interlayer -- comprising gelatin and 2,5-di-sec-dodecylhydroquinone antistain agent.

Layer 7 Yellow Filter Layer -- comprising yellow colloidal silver and gelatin.

Layer 8 Slow Yellow Layer -- comprising blue-sensitized silver bromoiodide grains, gelatin, a yellow dye-forming coupler and the antistain agent 5-sec-octadecylhydroquinone-2-sulfonate, potassium salt.

Layer 9 Fast Yellow Layer -- comprising a faster blue-sensitized silver bromoiodide grains,

gelatin, a yellow dye-forming coupler and the antistain agent 5-sec-octadecylhydroquinone-2-sulfonate, potassium salt.

Layer 10 UV Absorbing Layer -- comprising a UV absorber 3-(di-n-hexylamino)allylidenemalononitrile and gelatin.

Layer 11 Protective Overcoat Layer -- comprising gelatin and bis(vinylsulfonylmethyl)ether.

The silver halide emulsions in each color image-forming layer of this coating contained polydisperse, low aspect ratio grains of the type described in U.S. Patent 3,320,069. The emulsions were all optimally sensitized with sulfur and gold in the presence of thiocyanate and were spectrally sensitized to the appropriate regions of the visible spectrum. The emulsion utilized in the Fast Magenta Layer was a polydisperse (0.5 to 1.5 μm) low aspect ratio (≈3:1) silver bromoiodide (12 M% iodide) emulsion which was prepared in a manner similar to Emulsion No. 6 described above.

A second multicolor image-forming photographic element was prepared in the same manner except the Fast Magenta Layer utilized a tabular grain silver bromoiodide (8.4 M% iodide) emulsion in place of the low aspect ratio emulsion described above. The emulsion had an average tabular grain diameter of about 2.5 μm, a tabular grain thickness of less than or equal to 0.12 μm, and an average tabular grain aspect ratio of greater than 20:1, and the projected area of the tabular grains was greater than 75 percent, measured as described above. The high and low aspect ratio emulsions were both similarly optimally chemically and spectrally sensitized.

Both photographic elements were exposed for 1/50 second through a multicolor 0-3.0 density step tablet (plus 0.60 neutral density) to a 600W 5500°K tungsten light source. Processing was for 3-1/4 minutes in a color developer of the type described in the British Journal of Photography Annual, 1979, pp. 204-206. Sensitometric results are given in Table II below.

TABLE II

Comparison of Tabular (High Aspect Ratio) and Three-Dimensional (Low Aspect Ratio) Grain Emulsions in Multilayer, Multicolor Image-Forming Elements

Fast Magenta Layer	Red	Green		Blue
	Log Speed	Log Speed	rms.* Gran.	Log Speed
Control	225	220	0.011	240
Example	225	240	0.012	240

*Measured at a density of 0.25 above fog; 48 µm aperture.

The results in the above Table II illustrate that the tabular grains of the present invention provided a substantial increase in green speed with very little increase in granularity.

D. Speed/Granularity of Black-and-White Photographic Materials

To illustrate speed/granularity advantage in black-and-white photographic materials five of the chemically and spectrally sensitized emulsions described above, Emulsion Nos. 1, 4, 5, 6, and 7, were coated on a poly(ethylene terephthalate) film support. Each coated element comprised a silver halide emulsion at 3.21 g silver/m^2 and gelatin at 4.16 g/m^2 to which had been added the antifoggant 4-hydroxy-6-methyl-1,3,3a-7-tetraazaindene at 3.6 g/mole silver. An overcoat layer, comprising gelatin

at 0.88 g/m^2 and the hardener bis(vinylsulfonyl-methyl)ether at 1.75 percent based on total gelatin weight, was applied.

The resulting photographic elements were exposed for 1/100 of a second through a 0-3.0 density step tablet plus a Wratten No. 9 filter and a 1.26 density neutral filter, to a 600W, 3000°K tungsten light source. The exposed elements were then developed in an N-methyl-p-aminophenol sulfate-hydroquinone (Kodak DK-50) developer at 20°C, the low aspect ratio emulsions were developed for 5 minutes while the high aspect ratio emulsions were developed for 3.5 minutes to achieve matched curve shape for the comparison. (The words "Kodak" and "Wratten" are trade marks). The resulting speed and granularity measurements are shown on a plot of Log Green Speed vs. rms granularity X 10 in Figure 4. The speed- granularity relationships of Control Emulsions 5, 6, and 7 were clearly inferior to those of the Emulsions 1 and 4 of this invention.

Example Relating to Tabular Grain Emulsions Doped with Noble Metals of Group VIII of the Periodic Chart of the Elements

Emulsion A

An 0.8 μm average grain size low aspect ratio (<3:1) AgBrI (1 mole percent iodide) emulsion was prepared by a double-jet precipitation technique similar to that described in U.S. Patent 3,320,069, and had 0.12 mg/mole silver ammonium hexachloro-rhodate(III) present during the formation of the silver halide crystals. The emulsion was then chemically sensitized with 4.4 mg/mole silver of sodium thiosulfate pentahydrate, 1.75 mg/mole silver of potassium tetrachloroaurate, and 250 mg/mole silver of 4-hydroxy-6- methyl-1,3-3a,7-tetraazaindene for 23 mins at 60°C. Following chemical sensitization, the emulsion was spectrally sensitized with 87 mg/mole

silver anhydro-5,6-dichloro-1,3'-diethyl-3-(3-sulfopropyl)benzimidazoloxacarbocyanine hydroxide.

The low aspect ratio AgBrI emulsion was coated at 1.72 g silver/m^2 and 4.84 g gelatin/m^2 over a titanium dioxide-gelatin (10:1) layer on a paper support. The emulsion layer contained 4.65 g/mole silver of 4-hydroxy-6-methyl-1,3,3a,7- tetraazaindene. An overcoat was placed on the emulsion layer, consisting of 0.85 g gelatin/m^2.

Emulsion B

To 4.5 liters of a 1.5 percent gelatin, 0.17 M potassium bromide solution at 55°C, were added with stirring and by double-jet 2.34 M potassium bromide and 2.0 M silver nitrate solutions over a period of two minutes while maintaining a pBr of 0.8 (consuming 1.6 percent of the total silver nitrate used). The bromide solution was stopped and the silver nitrate solution continued for approximately 11 minutes at a rate consuming 8.5 percent of the total silver nitrate used until a pBr of 1.1 was attained. After 8 minutes 0.1 mg/mole Ag (based on final weight of silver) of ammonium hexachlororhodate was added to the reaction vessel. When the pBr of 1.1 was attained, a 2.14 M potassium bromide solution which was also 0.022 M in potassium iodide was double-jetted with the silver nitrate solution for approximately 22 minutes while maintaining pBr at 1.1, in an accelerated flow (4.3X from start to finish) and consuming 77.9 percent of the total silver nitrate used. To the emulsion was then added a 2.0 M $AgNO_3$ solution until a pBr of 2.7 was attained (consuming 12.0 percent of the total silver nitrate used). The total silver nitrate consumed was approximately 5 moles. The emulsion was cooled to 35°C, a solution of 200 g of phthalated gelatin in

1.0 liter of water was added and the emulsion was washed by the coagulation method.

The resulting tabular grain silver bromoiodide (1 M% iodide) emulsion had an average tabular grain diameter of 1.5 μm and an average tabular grain thickness of 0.08 μm. The tabular grains exhibited an average aspect ratio of 19:1 and accounted for 90 percent of the projected area of the total grain population. The tabular grain emulsion was then chemically sensitized with 5 mg/mole silver of sodium thiosulfate pentahydrate and 5 mg/mole silver of potassium tetrachloroaurate for 30 minutes at 65°C to obtain an optimum finish. Following chemical sensitization, the tabular grain emulsion was spectrally sensitized with 150 mg/mole silver of anhydro-5,6- dichloro-1,3'-diethyl-3-(3-sulfopropyl)benzimidazoloxacarbocyanine hydroxide. The tabular grain emulsion, Emulsion B, was then coated in the same manner as described above for Emulsion A.

Exposure and Process

The two coatings described above were exposed on an Edgerton, Germeshausen, and Grier sensitometer at 10^{-4} sec using a graduated density step tablet and a 0.85 density neutral filter. The step tablet had 0-3.0 density with 0.15 density steps.

The exposed coatings were then developed in a hydroquinone-1-phenyl-3-pyrazolidone black-and-white developer. Following fixing and washing, the coatings were submitted for densitometry, the results are shown in Table III below:

TABLE III

Rhodium-Doped Tabular Grain AgBrI Emulsion versus Rhodium-Doped AgBrI Emulsion of Low Aspect Ratio

Emulsion	Silver Coverage (g/m^2)	Relative Speed	Contrast	D_{max}	D_{min}
A Control	1.72	100	2.28	1.52	0.06
B Tabular Grain	1.61	209	2.20	1.75	0.10

As illustrated in Table III, the rhodium-doped AgBrI tabular grain emulsion coated at a lower silver coverage exhibited a 0.23 units higher maximum density and was faster than the control by 109 relative speed units (0.32 log E). Contrast of the two coatings was nearly equivalent.

Examples Illustrating Increased Speed Separation of Spectrally Sensitized and Native Sensitivity Regions

Four multicolor photographic elements were prepared, hereinafter referred to as Structures I through IV. Except for the differences specifically identified below, the elements were substantially identical in structure.

Structure I	Structure II	Structure III	Structure IV
Exposure	Exposure	Exposure	Exposure
↓	↓	↓	↓
OC	OC	OC	OC
B	B	B	B
IL + YF	IL	IL	IL + YF
FG	FG	TFG	TFG
IL	IL	IL	IL
FR	FR	TFR	TFR
IL	IL	IL	IL
SG	SG	SG	SG
IL	IL	IL	IL
SR	SR	SR	SR

OC is a protective gelatin overcoat, YF is yellow colloidal silver coated at 0.69 g/m^2 serving as a yellow filter material, and the remaining terms are as previously defined in connection with Layer Order Arrangements I through V. The blue (B), green (G), and red (R) recording color-forming layer units lacking the T prefix contained low aspect ratio silver bromide or bromoiodide emulsions prepared as taught by U.S. Patent 3,320,069. Corresponding layers in the separate structures were of the same iodide content, except as specifically noted.

The faster tabular grain green-sensitive emulsion layers (identified by the prefix T in the above structures) contained a tabular grain silver bromoiodide emulsion prepared in the following manner:

To 2.25 liter of an aqueous 0.17 molar potassium bromide bone gelatin solution (1.5 percent by weight gelatin) (Solution A) at 80°C and pBr 0.77 were added simultaneously by double-jet addition over a two minute period at a constant flow rate (consuming 0.61 percent of the total silver nitrate) aqueous 2.19 M potassium bromide and 2.0 M silver

nitrate solutions (Solutions B-1 and C-1, respectively).

After the initial two minutes, Solution B-1 was halted while Solution C-1 was continued until pBr 1.00 at 80°C was attained (2.44% of total silver nitrate used). An aqueous phthalated gelatin solution (0.4 liter of 20 percent by weight gelatin solution) containing potassium bromide (0.10 molar, Solution D) was added next at pBr 1.0 and 80°C.

Solutions B-1 and C-1 were added then to the reaction vessel by double-jet addition over a period of 24 minutes (consuming 44 percent of the total silver nitrate) at an accelerated flow rate (4.0X from start to finish). After 24 minutes Solution B-1 was halted and Solution C-1 was continued until pBr 1.80 at 80°C was attained.

Solution C-1 and an aqueous solution (Solution B-2) of potassium bromide (2.17 molar) and potassium iodide (0.03 molar) were added next to the reaction vessel by double-jet addition over a period of 12 minutes (consuming 50.4 percent of the total silver nitrate) at an accelerated flow rate (1.37X from start to finish).

Aqueous solutions of potassium iodide (0.36 molar, Solution B-3) and silver nitrate (2.0 molar, Solution C-2) were added next by double-jet addition at a constant flow rate until pBr 2.16 at 80°C was attained (2.59% of total silver nitrate consumed). 6.57 Moles of silver nitrate were used to prepare this emulsion.

The emulsion was cooled to 35°C, combined with 0.30 liter of aqueous phthalated gelatin solution (13.3 percent by weight gelatin) and coagulation washed twice.

The resulting tabular grain silver bromoiodide emulsion had an average tabular grain diameter

of 5.0 μm and an average tabular grain thickness of about 0.11 μm. The tabular grains accounted for about 90 percent of the total grain projected area and exhibited an average aspect ratio of about 45:1.

The emulsion was then optimally spectrally and chemically sensitized through the addition of 350 mg/mole Ag of anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt, 101 mg/mole Ag of anhydro-11-ethyl-1,1'-bis(3-sulfopropyl)-naph[1,2-d]oxazolocarbocyanine hydroxide, sodium salt, 800 mg/mole Ag of sodium thiocyanate, 6 mg/mole Ag of sodium thiosulfate pentahydrate and 3 mg/mole Ag of potassium tetrachloroaurate.

The faster tabular grain red-sensitive emulsion layer contained a tabular grain silver bromoiodide emulsion prepared and optimally sensitized in a manner similar to the tabular grain green-sensitized silver bromoiodide emulsion described directly above, differing only in that 144 mg/mole Ag of anhydro-5,6-dichloro-1-ethyl-3-(3-sulfobutyl)-3'-(3-sulfopropyl)benzimidazolonaphtho-[1,2-d]-thiazolocarbocyanine hydroxide and 224 mg/mole Ag of anhydro-5,5'-dichloro-3,9- diethyl-3'-(3-sulfobutyl)-thiazarbocyanine hydroxide were utilized as spectral sensitizers. The faster green- and red-sensitive emulsion layers of Structures I and II contained 9 mole percent iodide while the faster tabular grain green- and red-sensitive emulsions of Structures III and IV contained 1.5 and 1.2 mole percent iodide, respectively.

Other details relating to Structures I through IV will be readily apparent from U.S. Patent 4,184,876.

Structures I through IV were identically exposed with a 600 watt 2850°K source at 1/100 second

using a Daylight 5 filter and a 0 to 4 density step tablet having 0.20 density steps. Separate samples of Structures I through IV were exposed as described above, but with the additional interposition of a Wratten 98 filter to obtain blue exposures. Separate samples of Structures I through IV were exposed as described above, but with the additional interposition of a Wratten 9 filter to obtain minus blue exposures. All samples were identically processed using the C-41 Color Negative Process described in British Journal of Photography Annual, 1979, p. 204. Development was for 3 minutes 15 seconds at 38°C. Yellow, magenta, and cyan characteristic curves were plotted for each sample. Curves from different samples were compared by matching minimum density levels, that is, by superimposing the minimum density portions of the curves.

Results are summarized in Table IV.

Table IV

	Structures			
	I	II	III	IV
Green Structure Differences	FG	FG	TFG	TFG
Red Structure Differences	FR	FR	TFR	TFR
Yellow Filter	Yes	No	No	Yes
Log E Blue/Minus Blue Speed Differences				
Δ (A)	1.3	0.55	0.95	1.75
Δ' (B)	1.9	0.95	1.60	>2.40
Δ'' (C)	1.8	0.95	1.35	2.25
Δ''' (D)	2.5	1.55	2.20	>3.10

Δ is the difference in the log of the blue speed of the blue recording color-forming unit and the log of the blue speed of the green recording color-forming unit, as determined by Equation (A) above; $\Delta = (B_{W98} - G_{W98}) - (B_N - G_N)$;

Δ' is the difference in the log of the blue speed of the blue recording color-forming unit and the log of the blue speed of the red recording color-forming unit, as determined by Equation (B) above; $\Delta' = (B_{W98} - R_{W98}) - (B_N - R_N)$;

Δ'' is the difference in the log of the green speed of the green recording color-forming unit and the log of the blue speed of the green recording color-forming unit, as determined by Equation (C) above; $\Delta'' = G_{W9} - G_{W98}$; and

Δ''' is the difference in the log of the red speed of the red recording color-forming unit and the log of the blue speed of the red recording color-forming unit, as determined by Equation (D) above; $\Delta''' = R_{W9} - R_{W98}$.

In comparing Structures II and III, it can be seen that superior speed separations are obtained with Structure III employing tabular grains according to the present invention. Although Structure III did not attain the speed separations of Structure I, Structure III did not employ a yellow filter material and therefore did not encounter the disadvantages already discussed attendant to the use of such materials. Although Structure IV employed larger amounts of yellow filter material than necessary for use in the photographic elements of this invention, Structure IV does show that the speed separations of Structure III could be increased, if desired, by employing even small yellow filter densities.

A monochrome element was prepared by coating the faster green-sensitized tabular grain emulsion layer composition, described above, on a film support and overcoating with a gelatin protective layer. The blue to minus blue speed separation of the element was then determined using the exposure and processing techniques described above. The quantitative

difference determined by Equation (C), $\Delta'' = G_{W9} - G_{W98}$, was 1.28 Log E. This illustrates that adequate blue to minus blue speed separation can be achieved according to the present invention when the high aspect ratio tabular grain minus blue recording emulsion layer lies nearest the exposing radiation source and is not protected by any overlying blue absorbing layer.

Examples Relating to Improved Image Sharpness in Multilayer Photographic Elements Containing Tablular Grain Emulsions

The following three examples illustrate the improved image sharpness which is achieved by the use of high aspect ratio tabular grain emulsions in photographic materials. In these examples the control elements utilize low aspect ratio silver bromoiodide emulsions of the type described in U.S. Patent 3,320,069. For the purpose of these examples the low aspect ratio emulsions will be identified as conventional emulsions, their physical properties being described in Table V.

TABLE V

Conventional Emulsion No.	Average Grain Diameter	Average Aspect Ratio
C1	1.1 μm	3:1
C2	0.4-0.8 μm	3:1
C3	0.8 μm	3:1
C4	1.5 μm	3:1
C5	0.4-0.5 μm	3:1
C6	0.4-0.8 μm	3:1

Four tabular grain (high aspect ratio) silver bromoiodide emulsions were prepared by methods similar to those described in the examples relating to speed/granularity improvements (emulsions Nos. 1

to 4). The physical properties of these emulsions are described in Table VI.

TABLE VI

Tabular Grain Emulsion No.	Tabular Grain Approximate Average Diameter	Tabular Grain Thickness	Tabular Grain Approximate Average Aspect Ratio	Tabular Grain % of Projected Area
T1	7.5 μm	≈0.19μm	40:1	≈65
T2	3.0 μm	≈0.07μm	40:1	>50
T3	2.4 μm	≈0.09μm	27:1	>70
T4	1.6 μm	≈0.06μm	27:1	>70

The silver bromoiodide emulsions described above (C1-C6 and T1-T4) were then coated in a series of multilayer elements. The specific variations are shown in the tables containing the results. Although the emulsions were chemically and spectrally sensitized, sensitization is not essential to produce the sharpness results observed.

Common Structure A

Overcoat Layer
Fast Blue-Sensitive, Yellow Dye-Forming Layer
Slow Blue-Sensitive, Yellow Dye-Forming Layer
Interlayer (Yellow Filter Layer)
Fast Green-Sensitized, Magenta Dye-Forming Layer
Interlayer
Fast Red-Sensitized, Cyan Dye-Forming Layer
Interlayer
Slow Green-Sensitized, Magenta Dye-Forming Layer
Interlayer
Slow Red-Sensitized, Cyan Dye-Forming Layer
/ / / / / S U P P O R T / / / / /

Exposure and Processing

The samples were exposed and developed as described hereinafter. The sharpness determinations were made by determining the Modulation Transfer Functions (MTF). This method is known in the art, see for example, Journal of Applied Photographic Engineering, 6 (1):1-8, 1980.

Modulation Transfer Functions for red light were obtained by exposing the multilayer coatings for 1/15 sec at 60 percent modulation using a Wratten 29 and an 0.7 neutral density filter. Green MTF's were obtained by exposing for 1/15 sec at 60 percent modulation in conjunction with a Wratten 99 filter.

Processing was through the C-41 Color Negative Process as described in British Journal of Photography Annual 1979, p. 204. Development time was 3-1/4 min at 38°C (100°F). Following process, Cascaded Modulation Transfer (CMT) Acutance Ratings at 16 mm magnification were determined from the MTF curves.

Results

The composition of the control and experimental coatings along with CMT acutance values for red and green exposures are shown in Table VII.

TABLE VII

Sharpness of Structure A Varied in Conventional and Tabular Grain Emulsion Layer Content

Coating No.	1	2	3	4	5	6	7
FY	C1	C1	T-1	T-1	T-1	T-1	T-1
SY	C2	C2	T-2	T-2	T-2	T-2	T-2
FM	C3	T-3	T-3	T-3	C3	T-2	T-2
FC	C4	C4	C4	C4	C4	C4	T-2
SM	C5	T-4	T-4	C5	C5	C5	C5
SC	C6	C6	C6	C6	C6	C6	C6
Red CMT Acutance	79.7	78.7	82.7	84.0	83.1	85.3	86.3
Δ CMT Units	---	-1.0	+3.0	+4.3	+3.4	+5.6	+6.6
Green CMT Acutance	86.5	87.8	93.1	92.8	90.1	92.8	92.1
Δ CMT Units	---	+2.3	+6.6	+6.3	+3.6	+6.3	+5.6

Unexpectedly, as shown in Table VII, placing tabular grain emulsions in multilayer color coatings can lead to a <u>decrease</u> in sharpness. Considering Red CMT Acutance, one observes that Coating 2, containing <u>two</u> tabular grain layers, is less sharp (-1.0 CMT units) than control Coating 1, an all conventional emulsion structure. Similarly, Coating 3 (four tabular grain layers) is less sharp than Coating 4 (three tabular grain layers) by 1.3 CMT units and less sharp than Coating 5 (two tabular grain layers) by 0.4 CMT units. However, Coatings 6 and 7 demonstrate that by proper placement of specific tabular grain emulsions (note that Coating 6 is sharper in Red CMT Acutance than Coating 4 by 1.3 units) in layers nearest the source of exposing radiation, very significant improvements can be

obtained over the control coating containing all conventional emulsions. As seen in the above table, Coating 6 is 6.3 green CMT units sharper than Coating 1, and Coating 7 is 6.6 Red CMT units sharper than Coating 1.

Common Structure B

Overcoat Layer
Fast Blue-Sensitive, Yellow Dye-Forming Layer
Slow Blue-Sensitive, Yellow Dye-Forming Layer
Interlayer (Yellow Filter Layer)
Fast Green-Sensitized, Magenta Dye-Forming Layer
Slow Green-Sensitized, Magenta Dye-Forming Layer
Interlayer
Fast Red-Sensitized, Cyan Dye-Forming Layer
Slow Red-Sensitized, Cyan Dye-Forming Layer
Interlayer
/ / / / / S U P P O R T / / / / /

After coating, the multicolor photographic elements of Common Structure B were exposed and processed according to the procedure described in the preceding example. The composition variations of the control and experimental coatings along with CMT acutance ratings are shown in Table VIII.

TABLE VIII

Sharpness of Structure B Varied in Conventional and Tabular Grain Emulsion Layer Content

Coating No.	1	2	3	4
FY	C1	C1	T-1	T-1
SY	C2	C2	T-2	T-2
FM	C3	T-3	T-3	C3
SM	C5	T-4	T-4	C5
FC	C4	C4	C4	C4
SC	C6	C6	C6	C6
Red CMT Acutance	80.0	78.4	83.9	82.8
Δ CMT Units	---	-1.6	+3.9	+2.8
Green CMT Acutance	87.3	88.9	94.3	92.3
Δ CMT Units	---	+1.6	+7.0	+5.0

The data presented in Table VIII illustrates beneficial changes in sharpness in photographic materials which can be obtained through the use of tabular grain emulsions lying nearest the source of exposing radiation and detrimental changes when the tabular grain emulsions in intermediate layers underlie light scattering emulsion layers.

Common Structure C

Fast Magenta
Slow Magenta
/ / / / / SUPPORT / / / / /

Two monochrome elements, A (Control) and B (Example), were prepared by coating fast and slow magenta layer formulations on a film support.

TABLE IX

Emulsions		
Element A	Element B	Layer
C3	T3	Fast Magenta
C5	T4	Slow Magenta

The monochrome elements were then evaluated for sharpness according to the method described for the previous examples, with the following results.

TABLE X

Element	CMT Acutance (16 mm)
A (Control)	93.9
B (Tabular Grain Emulsion)	97.3

Example Illustrating Reduced High-Angle Scattering by High Aspect Ratio Tabular Grain Emulsions

To provide a specific illustration of the reduced high-angle scattering of high aspect ratio tabular grain emulsions according to this invention as compared to nontabular grain emulsions of the same average grain volume, the quantitative angular light scattering detection procedure described above with reference to Figure 5 was employed. The high aspect ratio tabular grain emulsion according to the present invention consisted of dispersing medium and tabular grains having an average diameter of 5.4 micrometers and an average thickness of 0.23 micrometer and an average aspect ratio of 23.5:1. Greater than 90% of the projected area of the grains was provided by the tabular grains. The average grain volume was 5.61 cubic micrometers. A control nontabular emulsion was employed having an average grain volume of 5.57 cubic micrometers. (When resolved into spheres of the same volume--i.e., equivalent spheres--both emulsions had nearly equal grain diameters.) Both emulsions had a total transmittance of 90 percent when they were immersed in a liquid having a matching refractive

index. Each emulsion was coated on a transparent support at a silver coverage of 1.08 g/m^2.

As more specifically set forth below in Table XI, lower percentages of total transmitted light were received over the detection surface areas subtended by ϕ up to values of ϕ of 90° with the high aspect ratio tabular grain emulsion of this invention as compared to the control emulsion of similar average grain volume. From Table XI it is also apparent that the collection angle for both emulsions was substantially below 6°. Thus neither emulsion would be considered a turbid emulsion in terms of its light scattering characteristics. When ϕ was 70° the emulsion of the present invention exhibited only half of the high-angle scattering of the control emulsion.

Table XI

Percent of Transmitted Light Contained Within Angle Phi

ϕ	Tabular Grain Emulsion (Example)	Nontabular Grain Emulsion (Control)	Percent Reduction
30°	2%	6%	67%
50°	5%	15%	67%
70°	12%	24%	50%
80°	25%	33%	24%
84°	40%	40%	0%

Example Illustrating Blue Spectral Sensitization of A Tabular Grain Emulsion

A tabular grain silver bromoiodide emulsion (3 M% iodide) was prepared in the following manner:

To 3.0 liters of a 1.5 percent gelatin, 0.17 M potassium bromide solution at 60°C were added to with stirring and by double-jet, 4.34 M potassium bromide in a 3 percent gelatin solution and 4.0 M

silver nitrate solution over a period of 2.5 minutes while maintaining a pBr of 0.8 and consuming 4.8 percent of the total silver nitrate used. The bromide solution was then stopped and the silver nitrate solution continued for 1.8 minutes until a pBr of 1.3 was attained consuming 4.3 percent of the silver nitrate used. A 6 percent gelatin solution containing 4.0 M potassium bromide and 0.12 M potassium iodide was then run concurrently with the silver nitrate solution for 24.5 minutes maintaining pBr 1.3 in an accelerated flow (2.0X from start to finish) (consuming 87.1 percent of the total silver nitrate used). The bromide solution was stopped and the silver nitrate solution run for 1.6 minutes at a rate consuming 3.8 percent of the total silver nitrate used, until a pBr of 2.7 was attained. The emulsion was then cooled to 35°C, 279 g of phthalated gelatin dissolved in 1.0 liters of distilled water was added and the emulsion was coagulation washed. The resulting silver bromoiodide emulsion (3 M% iodide) had an average grain diameter of about 1.0 μm, a average thickness of about 0.10 μm, yielding an aspect ratio of about 10:1. The tabular grains accounted for greater than 85% of the total projected area of the silver halide grains present in the emulsion layer. The emulsion was chemically sensitized with sodium thiocyanate, sodium thiosulfate, and potassium tetrachloroaurate.

Coating 1 -- A portion of the chemically sensitized emulsion was coated on a cellulose triacetate film support. The emulsion coating was comprised of tabular silver bromoiodide grains (1.08 g Ag/m^2) and gelatin (2.9 g/m^2) to which had been added the magenta dye-forming coupler 1-(6-chloro-2,4-dimethylphenyl)-3-[α-(m-pentadecylphenoxy)-butyramido]-5-pyrazolone (0.79 g/m^2), 2-octadecyl-

5-sulfohydroquinone (1.69 g/mole Ag), and 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (3.62 g/mole Ag).

Coating 2 -- A second portion of the tabular grain silver bromoiodide emulsion was spectrally sensitized to blue light by the addition of 3 x 10^{-4} mole/mole Ag of anhydro-5,6-dimethoxy-5-methylthio-3,3'-di(3-sulfopropyl)thiacyanine hydroxide, triethylamine salt (λmax 490 nm). The spectrally sensitized emulsion was then constituted using the same magenta dye-forming coupler as in coating 1 and coated as above.

The coatings were exposed for 1/25 second through a 0-3.0 density step tablet to a 500W 5400°K tungsten light source. Processing was for 3 minutes in a color developer of the type described in the British Journal of Photography Annual, 1979, Pages 204-206.

Coating 2 exhibited a photographic speed 0.42 log E faster than Coating 1, showing an effective increase in speed attributable to blue sensitization.

Examples to Illustrate Properties of Silver Bromoiodides of Uniform Iodide Distribution

A. Emulsion Preparations

Emulsion 1 (Example)

To 30.0 liters of a well-stirred aqueous bone gelatin (0.8 percent by weight) solution containing 0.10 molar potassium bromide were added by double-jet addition at constant flow, a 1.20 molar potassium bromide and a 1.2 molar silver nitrate solution for 5 minutes at pBr 1.0 at 75°C thereby consuming 2.40 percent of the total silver used. A phthalated gelatin solution (2.4 liters, 20 percent by weight) was added to the reaction vessel and stirred for 1 minute at 75°C. The silver nitrate solution described above was added then at constant flow rate for approximately 5 minutes until

pBr 1.36 at 75°C was reached consuming 4.80 percent of the total silver used. An aqueous solution containing potassium bromide (1.06 molar) plus potassium iodide (0.14 molar) and an aqueous solution of silver nitrate (1.2 molar) were added by double-jet addition utilizing accelerated flow (2.4X from start to finish) at pBr 1.36 at 75°C for approximately 50 minutes until the silver nitrate solution was exhausted thereby consuming 92.8 percent of the total silver used. Approximately 20 moles of silver were used to prepare the emulsion. Following precipitation the emulsion was cooled to 35°C, 350 grams of additional phthalated gelatin were added, stirred well and the emulsion was washed three times by the coagulation process of Yutzy and Russell, U.S. Patent 2,614,929. Then 2.0 liters of bone gelatin solution (12.3 percent by weight) solution were added and the emulsion was adjusted to pH 5.5 and pAg 8.3 at 40°C.

The resultant silver bromoiodide (88:12) emulsion had an average tabular grain diameter of 2.8 μm, and thickness of 0.095 μm, and an average aspect ratio of 29.5:1. The tabular grains accounted for greater than 85% of the total projected area of the silver bromoiodide grains present in the emulsion.

Emulsion 2 (Example)

To 7.5 liters of a well-stirred bone gelatin (0.8 percent by weight) solution containing 0.10 molar potassium bromide were added by double jet, a 1.20 molar potassium bromide solution and a 1.20 molar silver nitrate solution at constant flow for 5 minutes at pBr 1.0/65°C consuming 2.4 percent of the total silver used. After adding an aqueous phthalated gelatin solution (0.7 liter, 17.1 percent by weight) the emulsion was stirred for 1 minute at 65°C. A 1.20 molar silver nitrate solution was

added at 65°C until pBr 1.36 was reached consuming 4.1 percent of the total silver used. A halide solution containing potassium bromide (1.06 molar) plus potassium iodide (0.14 molar) and a 1.20 molar silver nitrate solution were added by double-jet addition utilizing accelerated flow (2X from start to finish) for 52 minutes at pBr 1.36/65°C consuming 93.5 percent of the total silver used. Approximately 5.0 moles of silver were used to prepare this emulsion. Following precipitation the emulsion was cooled to 35°C, adjusted to pH 3.7 and washed by the process of Yutzy and Russell, US 2,614,929. Additional phthalated gelatin solution (0.5 liter, 17.6 percent by weight) was added; after stirring for 5 minutes the emulsion was cooled again to 35°C/pH 4.1 and washed by the Yutzy and Russell process. Then 0.7 liter of aqueous bone gelatin solution (11.4 percent by weight) was added and the emulsion was adjusted to pH 5.5 and pAg 8.3 at 40°C.

The resultant silver bromoiodide emulsion (88:12) had an average tabular grain diameter of 2.2 μm, and thickness of 0.11 μm and an average aspect ratio of 20:1. The tabular grains accounted for greater than 85% of the total projected area of the silver bromoiodide grains present in the emulsion.

Emulsion 3 (Example)

To 7.5 liters of a well-stirred bone gelatin (0.8 percent by weight) solution containing 0.10 molar potassium bromide were added by double-jet addition, a 1.20 molar potassium bromide solution and a 1.20 molar silver nitrate solution at constant flow for 5 minutes at pBr 1.0/55°C thereby consuming 2.40 percent of the total silver used. After adding a phthalated aqueous gelatin solution (0.7 liter, 17.1 percent by weight) and stirring for 1 minute at 55°C , a 1.20 molar solution of silver

nitrate was added at constant flow rate until pBr 1.36 was reached consuming 4.1 percent of the total silver used. A halide solution containing potassium bromide (1.06 molar) plus potassium iodide (0.14 molar) and a 1.20 molar silver nitrate solution were added by double-jet addition utilizing accelerated flow (2X from start to finish) for 52 minutes at pBr 1.36/55°C consuming 93.5 percent of the total silver used. Approximately 5.0 moles of silver were used to prepare this emulsion. Following precipitation the emulsion was cooled to 35°C, adjusted to pH 3.7 and washed by the process of Yutzy and Russell, US 2,614,929. Additional phthalated gelatin solution (0.5 liter, 17.6 percent by weight) was added; after stirring for 5 minutes the emulsion was cooled again to 35°C/pH 4.1 and washed by the Yutzy and Russell process. Then 0.7 liter of aqueous bone gelatin solution (11.4 percent by weight) and the emulsion was adjusted to pH 5.5 and pAg 8.3 at 40°C.

The resulting silver bromoiodide (88:12) emulsion had an average tabular grain diameter of 1.7 μm, and thickness of 0.11 μm and an average aspect ratio of 15.5:1. The tabular grains accounted for greater than 85% of the total projected area of the silver bromoiodide grains present in the emulsion.

Emulsion 4 (Example)

To 7.5 liters of a well-stirred bone gelatin (0.8 percent by weight) solution containing 0.10 molar potassium bromide were added by double-jet addition, a 1.20 molar potassium bromide solution and a 1.20 molar silver nitrate solution at constant flow for 2.5 minutes at pBr 1.0/55°C thereby consuming 2.40 percent of the total silver used. After adding an aqueous phthalated gelatin solution (0.7 liter, 17.1 percent by weight) and stirring for 1 minute at 55°C, a 1.20 molar solution

of silver nitrate was added at a constant flow rate until pBr 1.36 was reached consuming 4.1 percent of the total silver used. A halide salt solution containing potassium bromide (1.06 molar) plus potassium iodide (0.14 molar) and a 1.20 molar silver nitrate solution were added by double-jet addition utilizing accelerated flow (2X from start to finish) for 52 minutes at pBr 1.36/55°C consuming 93.5 percent of the total silver used. Approximately 5.0 moles of silver were used to prepare this emulsion. Following precipitation the emulsion was cooled to 35°C, adjusted to pH 3.7 and washed by the process of Yutzy and Russell, US 2,614,929. Additional phthalated gelatin solution (0.5 liter, 17.6 percent by weight) was added and the emulsion was redispersed at pH 6.0, 40°C. After stirring for 5 minutes the emulsion was cooled again to 35°C/pH 4.1 and washed by the Yutzy and Russell process. Then 0.7 liter of aqueous bone gelatin solution (11.4 percent by weight) was added and the emulsion was adjusted to pH 5.5 and pAg 8.3 at 40°C.

The resulting silver bromoiodide (88:12) emulsion had an average tabular grain diameter of 0.8 μm, and thickness of 0.08 μm and an average aspect ratio of 10:1. The tabular grains accounted for greater than 55% of the total projected area of the silver bromoiodide grains present in the emulsion.

Emulsion A (Control)

9.0 liters of an aqueous phthalated gelatin (1.07 percent by weight) solution which contained 0.045 molar potassium bromide, 0.01 molar potassium iodide, and 0.11 molar sodium thiocyanate was placed in a precipitation vessel and stirred. The temperature was adjusted to 60°C. To the vessel were added by double-jet addition a 1.46 molar potassium

bromide solution which contained 0.147 potassium iodide and a 1.57 molar silver nitrate solution for 40 minutes at a constant flow rate at 60°C consuming 4.0 moles of silver. At approximately 1 minute prior to completion of the run, the halide salt solution was halted. After precipitation, the emulsion was cooled to 33°C and washed two times by the coagulation process described in Yutzy and Frame, US 2,614,928. Then 680 ml of a bone gelatin (16.5 percent by weight) solution was added and the emulsion was adjusted to pH 6.4 at 40°C.

Emulsion B (Control)

This emulsion was prepared similarly as Emulsion A, except that the temperature was reduced to 50°C and the total run time was reduced to 20 minutes.

Emulsion C (Control)

This emulsion was prepared similarly as Emulsion A, except that the temperature was reduced to 50°C and the total run time was reduced to 30 minutes.

Emulsion D (Control)

This emulsion was prepared similarly as Emulsion A, except that the temperature was increased to 75°C. The total run time was 40 minutes.

The physical characteristics of the tabular grain and the control silver bromoiodide emulsions are summarized in Table XII.

Table XII

Emulsion	Grain Shape	Average Grain Diameter	Average Grain Thickness	Average Aspect Ratio	Projected Area % Tabular Grains
1	Tabular	2.8μm	0.095μm	29.5:1	>85
2	Tabular	2.2μm	0.11 μm	20:1	>85
3	Tabular	1.7μm	0.11 μm	15.5:1	>85
4	Tabular	0.8μm	0.08 μm	10:1	>55
A	Spherical	0.99μm	*	≈1:1	**
B	Spherical	0.89μm	*	≈1:1	**
C	Spherical	0.91μm	*	≈1:1	**
D	Spherical	1.10μm	*	≈1:1	**

* Estimated to be approximately equal to grain diameter.

** Tabular grains greater than 0.6 micron in diameter were essentially absent.

Each of Emulsions 1 through 4 and A through D contained 88 mole percent bromide and 12 mole percent iodide. In each of the emulsions the iodide was substantially uniformly distributed within the grains.

B. Dye Imaging Results

The tabular grain and control AgBrI emulsions were optimally chemically sensitized at pAg adjusted to 8.25 at 40°C according to the conditions listed in Table XIII. For the tabular grain emulsions spectral sensitization at pAg 9.95 at 40°C preceded the chemical sensitization while the control emulsions were optimally spectrally sensitized after chemical sensitization without further pAg adjustment. All values represent mg of sensitizer/Ag mole.

Table XIII

Emulsion	Chemical Sensitization (mg/Ag mole)* Gold	Sulfur	Thiocyanate	Hold	Spectral Sens.** Dye A
Tabular					
1	3.0	9.0	100	5'@60°C	700
2	4.0	12.0	100	0'@60°C	793
3	4.0	12.0	100	0'@65°C	800
4	5.0	15.0	100	5'@60°C	900
Control					
A	1.0	2.9	0	5'@65°C	210
B	1.1	3.2	0	5'@65°C	290
C	0.8	2.4	0	5'@65°C	233
D	0.5	1.5	0	5'@65°C	200

* Gold = potassium tetrachloroaurate
Sulfur = sodium thiosulfate pentahydrate
Thiocyanate = sodium thiocyanate

** Dye A = anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt

The differences in sensitization that appear in Table XIII were necessary to achieve optimum sensitization for each of the various emulsions. If the control emulsions had been chemically and spectrally sensitized identically to the tabular grain emulsions, their relative performance would have been less than optimum. To illustrate the results of identical sensitizations of the tabular grain and control emulsions, portions of Emulsion 2 and Emulsion C, hereinafter designated Emulsion 2x and Emulsion Cx, were identically chemically and spectrally sensitized as follows: Each emulsion was spectrally sensitized with 900 mg Dye A/Ag mole at pAg 9.95 at 40°C, adjusted to pAg 8.2 at 40°C and then chemically sensitized for 20 minutes at 65°C with 4.0 mg potassium tetrachloro-

aurate/Ag mole, 12.0 mg sodium thiosulfate pentahydrate/Ag mole, and 100 mg sodium thiocyanate/Ag mole.

The tabular grain and control AgBrI emulsions were separately coated in a single-layer magenta format on cellulose triacetate film support at 1.07 g silver/m^2 and 2.15 g gelatin/m^2. The coating element also contained a solvent dispersion of the magenta image-forming coupler 1-(2,4-dimethyl-6-chlorophenyl)-3-[α(3-n-pentadecylphenoxy)-butyramido]-5-pyrazolone at 0.75 g/m^2, the antifoggant 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, sodium salt at 3.6 g/Ag mole, and the antistain agent potassium 5-sec.-octadecylhydroquinone-2-sulfonate at 3.5 g/Ag mole. The coatings were overcoated with a 0.51 g/m^2 gelatin layer and were hardened at 1.5% bis(vinylsulfonylmethyl) ether based on the total gelatin content.

The coatings were exposed for 1/100 second to a 600W 3000°K tungsten light source through a 0-3.0 density step tablet plus Wratten No. 9 filter and 1.8 density neutral filter. Processing was for variable times between 1.5 and 6 minutes to achieve matched fog levels at 37.7°C in a color developer of the type described in the British Journal of Photography Annual, 1979, pages 204-206.

Both relative speed values and granularity measurements were independently taken at 0.25 density units above fog. A Log Green Speed vs. rms Granularity x 10^3 is shown in Figure 6. As illustrated, the tabular grain AgBrI emulsions consistently exhibited speed-granularity relationships superior to those exhibited by the control emulsions.

The speed-granularity relationships of Emulsions 2x and Cx in Figure 6 should be particu-

larly compared. Giving the tabular grain and control emulsions 2x and Cx identical chemical and spectral sensitizations as compared to individually optimized chemical and spectral sensitizations, as in the case of Emulsions 2 and C, an even greater superiority in the speed-granularity relationship of Emulsion 2x as compared to that of Emulsion Cx was realized. This is particularly surprising, since Emulsions 2x and Cx exhibited substantially similar average volumes per grain of 0.418 μm^3 and 0.394μm^3, respectively.

To compare the relative separations in minus blue and blue speeds of the example and control emulsions, these emulsions, sensitized and coated as described above, were exposed to the blue region of the spectrum was for 1/100 second to a 600W 3000°K tungsten light source through a 0-3.0 density step tablet (0.15 density steps) plus Wratten No. 36 + 38A filter and 1.0 density neutral filter. The minus blue exposure was the same except that a Wratten No. 9 filter was used in place of the Wratten No. 36 + 38A filter and the neutral filter was of 1.8 density units. Processing was for variable times between 1.5 and 6 minutes at 37.7°C in a color developer of the type described in the British Journal of Photography Annual, 1979, pages 204-206. Speed/fog plots were generated and relative blue and minus blue speeds were recorded at 0.20 density units above fog. Sensitometric results are given in Table XIV.

Table XIV

Emulsion	Δ Speed (Minus blue speed - blue speed)
Tabular	
1	+45*
2	+42
3	+43
4	+37
Control	
A	-5
B	+5
C	+0
D	-5

*30 relative speed units = 0.30 Log E

As illustrated in Table XIV the tabular grain AgBrI emulsions showed significantly greater minus blue to blue speed separation than the control emulsions of the same halide composition. These results demonstrate that optimally sensitized high aspect ratio tabular grain AgBrI emulsions in general exhibit increased sensitivity in the spectral region over optimally sensitized conventional AgBrI emulsions. If the iodide content is decreased, a much larger separation of minus blue and blue speeds can be realized, as has already been illustrated by prior examples.

Emulsions 1, 2, and 3 and Control Emulsions A, B, C and D were compared for sharpness. Sensitization, coating and processing was identical to that described above. Modulation transfer functions for green light were obtained by exposing the coatings at various times between 1/30 and 1/2 second at 60 percent modulation in conjunction with a Wratten No. 99 filter. Following processing, Cascaded Modulation Transfer (CMT) Acutance Ratings at 16 mm magnification were obtained from the MTF curves.

The example emulsions exhibited a green CMT acutance ranging from 98.6 to 93.5. The control emulsions exhibited a green CMT acutance ranging from 93.1 to 97.6. The green CMT acutance of Emulsions 2 and C, which had substantially similar volumes per grain, is set forth below in Table XV.

Table XV

	Green CMT Acutance
Example Emulsion 2	97.2
Control Emulsion C	96.1

C. Silver Imaging Results

The control emulsions were adjusted to pH 6.2 and pAg 8.2 at 40°C and then optimally chemically sensitized by adding sodium thiosulfate pentahydrate plus potassium tetrachloroaurate and holding the emulsions at a specified temperature for a period of time. The emulsions were spectrally sensitized by adding anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)-oxacarbocyanine hydroxide, sodium salt (Dye A) and anhydro-3-ethyl-9-methyl-3'-(3-sulfobutyl)thiocarbocyanine hydroxide (Dye B) at the specified amounts. (See Table XVI for details.)

The tabular grain emulsions were spectrally sensitized by adding Dyes A and B to the emulsions at pAg 9.95 at 40°C prior to chemical sensitization with sodium thiocyante, sodium thiosulfate pentahydrate and potassium tetrachloroaurate at a specified temperature for a period of time. (See Table XVI.)

Table XVI

Emulsion	*SCN/S/Au mg/mole Ag	Time/Temp min/°C	Dye A/Dye B mg/mole Ag	35 mm CMT
1	100/4.5/1.5	0/60	387/236	101.3
2	100/4.5/1.5	5/60	387/236	101.5
3	100/4.5/1.5	5/60	581/354	100.8
4	100/12/4	0/55	581/354	97.3
A	0/1.94/0.97	5/65	123/77	97.6
B	0/1.94/0.97	15/65	139/88	96.5
C	0/1.94/0.97	10/65	116/73	97.5
D	0/1.50/0.525	5/60	68.1/43	98.0

* SCN: Sodium Thiocyanate
S: Sodium Thiosulfate Pentahydrate
Au: Potassium Tetrachloroaurate

The emulsions were coated at 4.3 g Ag/m^2 and 7.53 g gel/m^2 on a film support. All coatings were hardened with mucochloric acid (1.0% by wt. gel). Each coating was overcoated with 0.89 g gel/m^2.

The procedure for obtaining Photographic Modulation Transfer Functions is described in Journal of Applied Photographic Engineering, 6(1):1-8, 1980.

Modulation Transfer Functions were obtained by exposing for 1/15 second at 60 percent modulation using a 1.2 neutral density filter. Processing was for 6 minutes at 20°C in an N-methyl-p-aminophenol sulfate-hydroquinone developer (Kodak Developer D-76). Following processing, Cascaded Modulation Transfer (CMT) Acutance ratings at 35 mm magnification were determined from the MTF curves. (See Table XVI.)

The data in Table XVI clearly demonstrate the improvement in sharpness obtainable with tabular grain emulsions in a black-and-white format.

To compare silver image speed-granularity relationships, separate portions of the coatings

described above were also exposed for 1/100 second to a 600W 5500°K tungsten light source through a 0-4.0 continuous density tablet and processed for 4, 6, and 8 minutes at 20°C in an N-methyl-p-aminophenol sulfate-hydroquinone developer (Kodak Developer D-76). Relative speed values were measured at 0.30 density units above fog and rms semispecular (green) granularity determinations were made at 0.6 density units above fog. A log speed vs rms semi-specular granularity plot for the 6 minute development time is given in Figure 7. The speed-granularity relationships of the tabular grain AgBrI emulsions were clearly superior to those of the AgBrI control emulsions. Development times of 4 and 8 minutes gave similar results. In those instances in which matched contrasts were not obtained, the tabular grain emulsions had higher contrasts. This had the result of showing the tabular grain emulsions of higher contrast to have a higher granularity than would have been the case if contrasts of the emulsions had been matched. Thus, although Figure 7 shows the tabular grain emulsions to be clearly superior to the control emulsions, to the extent the tabular grain emulsions exhibited higher contrasts than the control emulsions, the full extent of their speed-granularity relationship superiority is not demonstrated.

Example Illustrating the Performance of a 175:1 Aspect Ratio Emulsion

The high aspect ratio tabular grain silver bromoiodide emulsion employed in this example had an average tabular grain diameter of approximately 27 microns, an average tabular grain thickness of 0.156 micron, and an average aspect ratio of approximately 175:1. The tabular grains accounted for greater than 95 percent of the total projected area of the silver bromoiodide grains present.

The emulsion was chemically and spectrally sensitized by holding it for 10 min at 65°C in the presence of sodium thiocyanate (150 mg/mole Ag, anhydro-5,5-dichloro-3,3'-bis(3-sulfopropyl)thiacyanine hydroxide, triethylamine salt (850 mg/mole Ag), sodium thiosulfate pentahydrate (1.50 mg/mole Ag) and potassium tetrachloroaurate (0.75 mg/mole Ag).

The sensitized emulsion was combined with yellow image-forming coupler α-pivalyl-α-[4-(4-hydroxybenzene-sulfonyl)phenyl]-2-chloro-5-(n-hexadecanesulfonamido)-acetanilide (0.91 g/m^2), 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindine (3.7 g/mole Ag), 2-(2-octadecyl)-5-sulfohydroquinone, sodium salt (3.4 g/mole Ag) and coated at 1.35 g Ag/m^2 and 2.58 g gel/m^2 on 1 polyester film support. The emulsion layer was overcoated with a gelatin layer (0.54 g/m^2) containing bis(vinylsulfonylmethyl)ether (1.0% by weight total gel).

The dried coating was exposed (1/100 sec, 500W, 5500°K) through a graduated density step wedge with a 1.0 neutral density filter plus a Wratten 2B filter and processed for 4.5 min/37.8°C in a color developer of the type described in The British Journal of Photography Annual, 1979, pages 204-206. The element had a D_{min} of 0.13, a D_{max} of 1.45, and a contrast of 0.56.

CLAIMS

1. A photographic silver bromoiodide emulsion comprising a dispersing medium and tabular silver bromoiodide grains,

characterized in that tabular silver bromoiodide grains having a thickness of less than 0.5 micrometer and a diameter of at least 0.6 micrometer have an average aspect ratio of greater than 8:1 and account for at least 50% of the total projected area of the silver bromoiodide grains in the emulsion, aspect ratio being defined as the ratio of the diameter of a tabular grain to its thickness and the diameter of a grain being defined as the diameter of a circle having an area equal to the projected area of said grain.

2. A silver bromoiodide emulsion according to claim 1, characterized in that said tabular silver bromoiodide grains having a thickness of less than 0.3 micrometer account for at least 50% of the total projected area of grains in the emulsion.

3. A silver bromoiodide emulsion according to claims 1 or 2, characterized in that the average aspect ratio is at least 12:1.

4. A silver bromoiodide emulsion according to any one of claims 1 to 3, characterized in that the average aspect ratio is at least 20:1.

5. A silver bromoiodide emulsion according to any of claims 1 to 4, characterized in that the tabular silver bromoiodide grains having a thickness of less than 0.3 micrometer and a diameter of at least 0.6 micrometer have an average aspect ratio of greater than 8:1 and account for at least 70% of the total projected area of the silver bromoiodide grains in the emulsion.

6. A silver bromoiodide emulsion according to claim 5, characterized in that said tabular bromoiodide grains account for at least 90% of the

total projected area of the silver bromoiodide grains in the emulsion.

7. A silver bromoiodide emulsion according to any one of claims 1 to 6, characterized in that iodide is present in said silver bromoiodide grains in a concentration of from 0.05 to 40 mole percent.

8. A silver bromoiodide emulsion according to claim 7, characterized in that iodide is present in said silver bromoiodide grains in a concentration of from 0.1 to 20 mole percent.

9. A silver bromoiodide emulsion according to claim 1, characterized in that said silver bromoiodide grains are comprised of up to 15 mole percent iodide, and that said silver bromoiodide grains having a thickness of less than 0.3 micrometer and a diameter of at least 0.6 micrometer have an average aspect ratio in the range of from 20:1 to 50:1 and account for at least 90% of the total projected area of silver bromoiodide grains in the emulsion.

10. A process of preparing a photographic silver bromoiodide emulsion according to any one of claims 1 to 9 by introducing silver, bromide, and iodide salts into a reaction vessel containing at least a portion of the dispersing medium, characterized by

adjusting the pBr of the dispersing medium within the reaction vessel prior to introduction of the iodide salt to a level of from 0.6 to 1.6,

maintaining the reaction vessel substantially free of iodide prior to introduction of the silver and bromide salts, and

maintaining the pBr within the reaction vessel at a level of at least 0.6 during introduction of the iodide salts.

11. A process according to claim 10 characterized by the steps

1) adjusting the pBr of the dispersing medium within the reaction vessel to a level of from 1.1 to 1.6 prior to concurrent introduction of the silver, bromide and/or iodide salts,

2) maintaining the reaction vessel substantially free of iodide prior to concurrent introduction of the silver and bromide salts, and

3) maintaining the pBr within the reaction vessel at a level of at least 0.6 during said concurrent introduction of the silver, bromide and iodide salts.

12. A process according to claim 10 or 11, characterized in that the pBr within the reaction vessel is maintained in the range of 0.6 to 2.2 during the introduction of iodide salt.

13. A process according to any of claims 10-12, characterized in that a peptizer is introduced into the reaction vessel so that it is present during concurrent introduction of silver, bromide and/or iodide salts.

14. A process according to any one of claims 10 to 13, characterized in that the contents of the reaction vessel are maintained in the range of 30 to 90°C during concurrent introduction of silver, bromide and/or iodide salts.

15. A process according to any one of claims 10 to 13, characterized in that the contents of the reaction vessel are maintained in the range of 40 to 80°C during concurrent introduction of silver, bromide and/or iodide salts.

16. A process according to any one of claims 10 to 15, characterized in that prior to introduction of the iodide salt the pBr of the dispersing medium within the reaction vessel is adjusted to a level of 1.5 to 1.1

17. A process according to any one of claims 10 to 16, characterized in that the pBr within the reaction vessel is maintained in the range of 0.8 to 1.6 during the introduction of iodide salt.

18. A process according to any one of claims 10 to 17, characterized in that the silver salt and at least one of the bromide and iodide salts are introduced in the form of silver halide grains having an average diameter of less than 0.1 micrometer.

19. A process according to any one of claims 10 to 18, characterized in that the concentration of iodide within the reaction vessel is maintained below 0.5 mole percent of the total halide concentration in the reaction vessel prior to concurrent introduction of the silver and halide salts.

20. A photographic silver bromoiodide emulsion according to claim 1 substantially as described herein and with reference to the Examples.

21. A process of preparing a photographic silver bromoiodide emulsion according to claim 10 substantially as described herein and with reference to the Examples.

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Applicant:
Eastman Kodak Company (USA-New York) 343 State Street Rochester New York 14650 United States of America

Inventors:
John Anthony Haefner 410 Woodland Lane Webster New York 14580 United States of America

Herbert Seagwick Wilgus 6770 Dugway Road Conesus New York 14435 United states of America

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Address for Service: P.A.C. Baron, ~~H. Davis, R.J. Nunney~~, Kodak Limited, Patent Department ~~P A C Baron Kodak Limited Patents and Trade Marks Dept P O Box 114 190 High Holborn WC1V 7EA~~ Headstone Drive Harrold Middlesex HA1 4TY.

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