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54 **Reduced dispersity high aspect ratio tabular grain emulsions.**

57 A high aspect ratio silver bromiodide tabular grain emulsion is disclosed in which tabular grains having a thickness of less than 0.3 μm account for greater than 50 percent of the projected area of the total grain population and have an average aspect ratio of greater than 12. The coefficient of variation of the total grain population is unusually low when the high average aspect ratio of the tabular grains is taken into account.

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REDUCED DISPERSITY HIGH ASPECT RATIO TABULAR GRAIN EMULSIONS

This invention relates to the field of photography. More particularly, the invention is directed to improvements in radiation sensitive silver-halide emulsions.

In the late 1940's a transition in the manufacture of silver halide photographic products began away from the use of single jet emulsions toward to the use of double jet emulsions. The disadvantage of single jet emulsions was that they were poly-disperse. They contained a wide range of grain shapes and sizes. This was the direct result of running silver salts into a halide salt solution of fixed volume in the reaction vessel and thereby varying the ratio of silver to halide continuously throughout the emulsion make.

In double jet precipitation both the halide and silver salts are concurrently introduced into the reaction vessel. Thus, it is possible to produce a grain population of little or no variance in grain shape and a very narrow distribution of grain sizes. Silver halide emulsions having a low variance of grain sizes are referred to as monodisperse emulsions.

Monodisperse emulsions are recognized to offer a variety of photographic advantages. For example, a larger percentage of the grains in a monodisperse emulsion can be optimally sensitized as a result of their similar surface areas. Fine grain populations, which disproportionately contribute to light scattering and therefore image sharpness reduction, are restricted. Larger grain populations, which contribute disproportionately to image granularity, are restricted. The reproducibility of the emulsions and their photographic performance rises as dispersity is reduced. Contrast of a single monodisperse emulsion is higher than that of poly-disperse emulsion of the same mean grain size. Monodisperse emulsions are employed not only for photographic applications requiring higher contrast, but are also blended to achieve aim contrasts in photographic applications requiring relatively lower contrast, since a blended monodisperse emulsion retains photographic advantages over a poly-disperse emulsion of the same mean grain size and contrast.

Maternaghan U.S. Patents 4,150,994 and 4,184,878 are representative of early reported attempts to prepare tabular grain silver bromoiodide emulsions. Covering power advantages were postulated. Low coefficients of variation were reported for the emulsions. However, in retrospect this is not surprising, since from remakes and grain characterizations the average aspect ratios (most simply measured as mean grain diameter divided by mean grain thickness) of these emulsions are ap-

proximately 4:1.

Subsequent to Maternaghan, intensive investigations of high aspect ratio silver bromoiodide emulsions were reported as well as procedures for their preparation. The average tabular grain aspect ratios of these emulsions were in all instances greater than 8:1. Wilgus et al U.S. Patent 4,434,226, Kofron et al U.S. Patent 4,439,520, Solberg et al U.S. Patent 4,433,048, Daubendiek et al U.S. Patent 4,414,310, Jones et al U.S. Patent 4,478,929, Evans et al U.S. Patent 4,504,570, and Maskasky U.S. Patent 4,435,501 are representative of the earliest published teachings relating to high aspect ratio silver bromoiodide emulsions. More recently Daubendiek et al U.S. Patent 4,693,964 and 4,672,027 have reported the preparation of high aspect ratio silver bromoiodide emulsions of much smaller mean grain diameters, referred to as small, thin tabular grain silver bromoiodide emulsions. Maskasky U.S. Patent 4,713,320 illustrates the effect of gelatin methionine reduction on silver bromoiodide high aspect ratio tabular grain emulsion preparation.

The advantages of silver bromoiodide high aspect ratio tabular grain emulsions include an improved relationship between speed and granularity, sharper images—both in single and multilayer photographic elements, accelerated development, higher insensitivity to temperature variations during development, higher fixing rates, more favorable toning, higher covering power, an increased separation between minus blue (green or red) and blue speeds when spectrally sensitized to the minus blue portion of the spectrum, increased blue speed when spectrally sensitized to blue light, and a variety of other advantages observed in the context of specific photographic applications.

Although almost all silver bromoiodide high aspect ratio tabular grain emulsions are prepared by double jet precipitation techniques, difficulties were experienced from the outset in reducing the dispersity of the emulsions. Whereas regular grain emulsions produced by double jet precipitation (e.g., regular cubic or octahedral grain emulsions) can be readily prepared containing only the desired grain population, tabular grain emulsions are rarely prepared with only tabular grains present. Thus, having mixed populations of tabular and nontabular grains is one source of dispersity in tabular grain emulsions. The second source of dispersity is the dispersity variances within the tabular grain population itself, which is a function of the twinning followed by edge deposition growth pattern that distinguishes tabular grain emulsions from regular grain emulsions, wherein twinning is absent or rare

and deposition favors no particular set of crystal faces. Further, dispersity in tabular grain emulsions increases as the average aspect ratios of the tabular grains increases. Therefore, dispersity levels which are easily attained in lower aspect ratio tabular grain emulsions have not been attainable at higher aspect ratios.

Himmelwright U.S. Patent 4,477,565 and Sugimoto et al U.S. Patents 4,609,621, 4,656,120, and 4,665,012 are illustrative of follow-on disclosures of variations in the preparation of high aspect ratio tabular grain silver bromiodide emulsions.

It has been recognized from the outset of high aspect ratio tabular grain emulsion investigations that silver bromide tabular grain emulsions are much more readily prepared to exhibit both high aspect ratios and low levels of dispersity than corresponding silver bromiodide emulsions. Research Disclosure Vol. 232, Aug. 10, 1983, Item 23212, (Mignot French Patent 2,534,036 corresponding) produced by a ripening procedure tabular grain silver bromide emulsions of average aspect ratios of 10, 12, and 25.6 with coefficients of variation of 15, 16, and 28.4, respectively. Research Disclosure and its predecessor Product Licensing Index are publications of Kenneth Mason Publications, Ltd., Emsworth, Hampshire PO10 7DD, England. Saitou et al West German OLS 3,707,135 A1 employs double and single jet precipitation techniques to produce silver bromide emulsions which exhibit higher coefficients of variation at aspect ratios comparable to those of Mignot, even though Saitou et al reports coefficients of variations based solely on the tabular grain population.

It is an object of this invention to provide a high aspect ratio tabular grain emulsion comprised of a dispersing medium and silver bromiodide grains, wherein tabular silver bromiodide grains having a thickness of less than 0.3 μm account for greater than 50 percent of the projected area of the total silver bromiodide grain population and have an average aspect ratio of greater than 12 exhibit both the advantages of high aspect ratio tabular grain silver bromiodide emulsions and the art recognized advantages of monodispersity.

The emulsion is characterized in that the quotient of the average silver bromiodide tabular grain aspect ratio divided by the coefficient of variation of the total silver bromiodide grain population is greater than 0.7.

Prior to the present invention it has been necessary to compromise either the average tabular grain aspect ratio or the monodispersity of a silver bromiodide emulsion. With the present invention a superior relationship of grain dispersity and high tabular grain aspect ratios is realized.

The present invention is an improvement on

the teachings of Wilgus et al U.S. Patent 4,434,226, Kofron et al U.S. Patent 4,439,520, Solberg et al U.S. Patent 4,433,048, Daubendiek et al U.S. Patent 4,414,310, 4,693,964 and 4,672,027, Evans et al U.S. Patent 4,504,570, and Maskasky U.S. Patents 4,435,501 and 4,713,320. All features of the emulsions of this invention, their preparation, and their photographic applications, except as otherwise indicated, are to be understood as being as described by these incorporated teachings.

The present invention is directed to silver bromiodide tabular grain emulsions which exhibit an improved relationship of grain tabularity to dispersity. A detailed discussion requires more definitive terms.

As herein employed the term "high aspect ratio tabular grain emulsion" refers to an emulsion in which the tabular grains having a thickness of less than 0.3 μm have an average aspect ratio of greater than 12 and account for greater than 50% of the total grain projected area. The average aspect ratio of the tabular grains can be determined by determining the aspect ratio of each grain and averaging the aspect ratios of all tabular grains or by dividing the average diameter of all of the tabular grains by the average thickness of all the tabular grains.

The term "coefficient of variation" is employed in its art recognized sense as 100 times the standard deviation of all silver bromiodide grain diameters divided by the average silver bromiodide grain diameter. All grains, including both tabular and nontabular grains, are counted in arriving at averages. Defined in this way, the coefficients of variation reported have higher numerical values than those based solely on the tabular grain population.

When the average aspect ratio of the tabular silver bromiodide grains of an emulsion of this invention is divided by the coefficient of variation of all of the silver bromiodide grains present, a quotient of greater than 0.7 is obtained. This is a significantly higher quotient than is exhibited by any silver bromiodide tabular grain emulsion heretofore known in the art. As shown in the examples below quotients of greater than 0.7, 0.8 and 1.0 can be realized by emulsion preparation procedures that have not been rigorously optimized. By routinely optimizing the emulsion preparation techniques of the examples in view of the general teachings of this specification it is recognized that quotients of 1.1, 1.5, 2.0, and higher are attainable.

The reason for defining the invention in terms of the quotient of the average aspect ratio divided by the coefficient of variation rather than simply in terms of a minimum coefficient of variation is that coefficients of variation increase linearly with increases in the average aspect ratios of tabular grains using comparable processes of emulsion

preparation. For silver bromiodide emulsions having average aspect ratios in the 5:1 to 10:1 range monodispersities acceptable for present photographic performance requirements are readily achieved. However, at average aspect ratios greater than 12:1 and beyond the art has an unsatisfied need for higher levels of monodispersity. The present invention makes possible an improved balance of tabular grain average aspect ratios and monodispersity in the aspect ratio ranges where satisfaction of desired monodispersity have not been heretofore realized.

The preferred emulsions of the invention are those in which the tabular silver bromiodide grains having a thickness of less than 0.3 μm (optimally less than 0.2 μm) have an average aspect ratio of greater than 12 (optimally at least 20). Very high average aspect ratios ranging up to 100 or more are contemplated. In the preferred form of the invention the tabular silver bromiodide grains satisfying the thickness criteria above account for greater than 70 percent (optimally greater than 90 percent) of the total silver bromiodide grain projected area. Ideally, of course, the emulsions of the invention consist essentially of tabular silver bromiodide grains satisfying the thickness criteria above.

To satisfy normal photographic image definition requirements the mean grain size (diameter) of the emulsions of this invention is less than 10 μm . While the invention can be employed to produce very small diameter (0.2 to 0.6 μm mean diameter) tabular grain emulsions, such as those disclosed by Daubendiek et al U.S. Patents 4,672,027 and 4,693,964, as well as those having mean tabular grain diameters above 0.6 μm , the present invention has particular preferred applicability to emulsions having mean grain diameters in the range of from 1.5 to 3.5 μm , particularly 1.5 to 2.5 μm .

The unique silver bromiodide grain population required by the tabular grain emulsions of this invention has resulted from replacing the empirical methods of emulsion preparation disclosed in the art by a strategy for grain nucleation and growth specifically devised to preserve monodispersity in the context of silver bromiodide tabular grain precipitation.

The strategy begins with dividing the emulsion precipitation process into three distinct stages:

(1) A nucleation stage in which all of the grains making up the emulsion come into existence as separate entities. This stage is specifically managed to minimize variance in the nuclei.

(2) A hold stage in which residual inequalities in grain nuclei are reduced.

(3) A growth stage in which residual inequalities in the grains, particularly at the onset of the growth stage, can be further reduced. The growth

stage is, of course, controlled so that continued formation of grain nuclei does not occur.

While a variety of specific techniques are available for implementing the precipitation strategies, not all are of equal importance nor are all required. It is a recognition of this invention that grain variance elimination at the earliest possible opportunity is of paramount importance, since an early grain variance has a cascading effect on all subsequent stages of emulsion preparation.

The most important single process variation for achieving emulsions satisfying the requirements of this invention is to implement a technique for as nearly concurrent formation of all of the grain nuclei as possible. In an aqueous solution supersaturated with silver and bromide ions precipitation occurs to produce a grain nucleus. This nucleus immediately begins to grow. Unless all nuclei are concurrently formed, the earlier formed nuclei will be larger than the initially formed nuclei. In the precipitation processes demonstrated in the examples for preparing emulsions satisfying the requirements of the invention the concentrations of the aqueous silver and bromide salts added to the reaction vessel are increased and the duration of their addition is condensed into a period of less than 10 seconds. Preferably both silver and bromide salt additions are completed in less than 5 seconds and ideally in less than 1 second. To accomplish this salt solution concentrations above 1 molar are preferred. This decreases the bulk of the materials to be introduced. Since the aim is to drive the silver and bromide ions out of solution as expeditiously as possible, temperature can be controlled to limit solubility. Whereas precipitation temperatures are known to range up to 90°C, it is preferred to limit temperatures at nucleation to 60°C or less. In summary, reducing the elapsed time of initial silver and bromide salt additions is the most important single process modification. Increasing salt concentrations and limiting temperature are preferred features of nucleation. Finally, iodide ion is preferably omitted from the nucleation stage to avoid unnecessarily complicating nucleation.

Upon creating the grains of the emulsion by nucleation, the next stage of the precipitation strategy is to reverse immediately the initial direction of net ion transfer from solution to nuclei, but in a controlled manner so that the majority of the nuclei remain. This is achieved by abruptly moving from a supersaturated solution to a solution which is below its silver and bromide ion saturation limit. The second stage is then a ripening stage in which the smaller silver halide nuclei disappear while the remaining nuclei remain. This can be achieved by employing any one or combination of known ripening procedures. The simplest of these is to adjust

upwardly the temperature of the nuclei emulsion, thereby raising the solubility level of the silver and bromide ions. It is also possible to increase the pBr of the solution while remaining within the growth ranges taught in the art for silver bromiodide tabular grain preparation. This lowers the bromide ion concentration in solution and induces bromide ion migration back into solution. It is a generally understood feature of ripening that smaller grains suffer a net loss of silver and bromide ions while remaining grains exhibit a net increase. As smaller grain nuclei are eliminated by ripening, the overall effect is to narrow the grain size frequency distribution.

In the extreme instance in which nucleation is conducted in the absence of a peptizer at room temperature the ripening can be conducted by raising the temperature up to 90° C, producing a temperature differential between nucleation and ripening of 70° C. In practice significant improvements in emulsion characteristics are achieved when the temperature differential between nucleation and ripening is in the range from about 10 to 40° C, optimally about 15 to 30° C.

The duration of ripening in the second stage is preferably from 5 to 30 minutes in the absence of a ripening agent other than the dissolved bromide ion. The addition of known ripening agents, such as thioethers, thiocyanate, ammonia, and the like, accelerate ripening. If ammonia is employed as a ripening agent, it is preferably deactivated at the end of the ripening interval by an appropriate pH adjustment. The nuclei ripening procedure of Notorf U.S. Patent 4,722,886 is specifically contemplated.

This procedure alone, however, will not produce the emulsions of this invention.

At the end of the ripening stage a grain nuclei population is present which exhibits less grain to grain variation than at the end of the nucleation step. It is now possible to grow emulsions satisfying the requirements of this invention by employing conventional silver bromiodide tabular grain growth conditions, such as those set forth in the teachings cited above.

Iodide ion is introduced in the growth stage. The teachings of Solberg et al U.S. Patent 4,433,048 disclose preferred considerations for iodide addition.

It is preferred that the pBr of the reaction vessel during both the ripening and growth stage be well above the pBr of the reaction vessel during nucleation. It is generally preferred to adjust the pBr of the reaction vessel at the outset of the ripening stage above 1.6 up to the growth stage pBr limits of the teachings cited above. Further increase of the pBr will result in deposition onto the major faces of the tabular grains and reduce the

average aspect ratio of the emulsion.

Modifying compounds can be present during silver bromiodide 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 precipitation, as illustrated by Arnold et al U.S. Patent 1,195,432, Hochstetter U.S. Patent 1,951,933, Trivelli et al U.S. Patent 2,448,060, Overman U.S. Patent 2,628,167, Mueller et al U.S. Patent 2,950,972, Sidebotham U.S. Patent 3,488,709, Rosecrants et al U.S. Patent 3,737,313, Berry et al U.S. Patent 3,772,031, Atwell U.S. Patent 4,269,927, and Research Disclosure, Vol. 134, June 1975, Item 13452. 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.

Once the silver bromiodide 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 Evams et al U.S. Patent 4,504,570.

In forming the tabular grain emulsions peptizer concentrations of from 0.2 to about 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 in the range of below about 6 percent, based on the total weight, prior to and during grain 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 about 5 to 50 grams of peptizer per mole of silver halide, preferably about 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 about 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. Pre-

ferred 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, gelatine—e.g., alkali-treated gelatin (cattle bone or hide gelatin) or acid-treated gelatin (pigskin gelatin), gelatin derivatives—e.g., acetylated gelatin, phthalated gelatin and the like, polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, agar-agar, arrowroot, albumin and the like as described in Yutzy et al U.S. Patents 2,614,928 and '929, Lowe et al U.S. Patents 2,691,582, 2,614,930, '931, 2,327,808 and 2,448,534, Gates et al U.S. Patents 2,787,545 and 2,956,880, Himmelmann et al U.S. Patent 3,061,436, Farrell et al U.S. Patent 2,816,027, Ryan U.S. Patents 3,132,945, 3,138,461 and 3,186,846, Dersch et al U.K. Patent 1,167,159 and U.S. Patents 2,960,405 and 3,436,220, Geary U.S. Patent 3,486,896, Gazzard U.K. Patent 793,549, Gates et al U.S. Patents 2,992,213, 3,157,506, 3,184,312 and 3,539,353, Miller et al U.S. Patent 3,227,571, Boyer et al U.S. Patent 3,532,502, Malan U.S. Patent 3,551,151, Lohmer et al U.S. Patent 4,018,609, Luciani et al U.K. Patent 1,186,790, Hori et al U.K. Patent 1,489,080 and Belgian Patent 856,631, U.K. Patent 1,490,644, UK. Patent 1,483,551, Arase et al U.K. Patent 1,459,906, Salo U.S. Patents 2,110,491 and 2,311,086, Fallesen U.S. Patent 2,343,650, Yutzy U.S. Patent 2,323,085, Lowe U.S. Patent 2,563,791, Talbot et al U.S. Patent 2,725,293, Hilborn U.S. Patent 2,748,022, DePauw et al U.S. Patent 2,956,883, Ritchie U.K. Patent 2,095, DeStubner U.S. Patent 1,752,069, Sheppard et al U.S. Patent 2,127,573, Liarg U.S. Patent 2,256,720, Gaspar U.S. Patent 2,361,936, Farmer U.K. Patent 15,727, Stevens U.K. Patent 1,062,116 and Yamamoto et al U.S. Patent 3,923,517.

When silver bromiodide high aspect ratio tabular grain emulsions according to the invention are being prepared in which the mean tabular grain thickness is less than about 0.07 μm , particularly less than 0.05 μm , it is preferred to employ gelatin and gelatin derived peptizers containing less than 30 micromoles per gram methionine. The methionine content can be reduced by treatment of the peptizer with an oxidizing agent, such as hydrogen peroxide. The teachings of Daubendiek et al U.S. Patents 4,672,027 and 4,693,964 are particularly applicable. Although not essential, the reduction or elimination of methionine from the peptizer facilitates achieving very thin tabular grain structures.

Other materials commonly employed in combination with hydrophilic colloid peptizers as vehicles (including vehicle extenders—e.g., materials in the form of latices) include synthetic polymeric

peptizers, carriers and/or binders such as poly(vinyl lactams), acrylamide polymers, polyvinyl alcohol and its derivatives, polyvinyl acetals, polymers of alkyl and sulfoalkyl acrylates and methacrylates; hydrolyzed polyvinyl acetates, polyamides, polyvinyl pyridine, acrylic acid polymers, maleic anhydride copolymers, polyalkylene oxides methacrylamide copolymers, polyvinyl oxazolidinones, maleic acid copolymers, vinylamine copolymers, methacrylic acid copolymers, acryloyloxyalkylsulfonic acid copolymers, sulfoalkylacrylamide copolymers, polyalkyleneimine copolymers, polyamines, N,N-dialkylaminoalkyl acrylates, vinyl imidazole copolymers, vinyl sulfide copolymers, halogenated styrene polymers, amineacrylamide polymers, polypeptides and the like as described in Hollister et al U.S. Patents 3,679,425, 3,706,564 and 3,813,251, Lowe U.S. Patents 2,253,078, 2,276,322, '323, 2,281,703, 2,311,058 and 2,414,207, Lowe et al U.S. Patents 2,484,456, 2,541,474 and 2,632,704, Perry et al U.S. Patent 3,425,836, Smith et al U.S. Patents 3,415,653 and 3,615,624, Smith U.S. Patent 3,488,708, Whiteley et al U.S. Patents 3,392,025 and 3,511,818, Fitzgerald U.S. Patents 3,681,079, 3,721,565, 3,852,073, 3,861,918 and 3,925,083, Fitzgerald et al U.S. Patent 3,879,205, Nottorf U.S. Patent 3,142,568, Houck et al U.S. Patents 3,062,674 and 3,220,844, Dann et al U.S. Patent 2,882,161, Schupp U.S. Patent 2,579,016, Weaver U.S. Patent 2,829,053, Alles et al U.S. Patent 2,698,240, Priest et al U.S. Patent 3,003,879, Merrill et al U.S. Patent 3,419,397, Stonham U.S. Patent 3,284,207, Lohmer et al U.S. Patent 3,167,430, Williams U.S. Patent 2,957,767, Dawson et al U.S. Patent 2,893,867, Smith et al U.S. Patents 2,860,986 and 2,904,539, Ponticello et al U.S. Patents 3,929,482 and 3,860,428, Ponticello U.S. Patent 3,939,130, Dykstra U.S. Patent 3,411,911 and Dykstra et al Canadian Patent 774,054, Ream et al U.S. Patent 3,287,289, Smith U.K. Patent 1,466,600, Stevens U.K. Patent 1,062,116, Fordyce U.S. Patent 2,211,323, Martinez U.S. Patent 2,284,877, Watkins U.S. Patent 2,420,455, Jones U.S. Patent 2,533,166, Bolton U.S. Patent 2,495,918, Graves U.S. Patent 2,289,775, Yackel U.S. Patent 2,565,418, Unruh et al U.S. Patents 2,865,893 and 2,875,059, Rees et al U.S. Patent 3,536,491, Broadhead et al U.K. Patent 1,348,815, Taylor et al U.S. Patent 3,479,186, Merrill et al U.S. Patent 3,520,857, Bacon et al U.S. Patent 3,690,888 Bowman U.S. Patent 3,748,143, Dickinson et al U.K. Patents 808,227 and '228, Wood U.K. Patent 822,192 and Iguchi et al U.K. Patent 1,398,055. These additional materials need not be present in the reaction vessel during precipitation, but rather are conventionally added to the emulsion prior to coating. 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 photographic elements, but also in other layers, such as overcoat layers, interlayers and layers positioned beneath the emulsion layers.

As discussed above, ripening can occur during the hold stage of emulsion preparation. However, ripening need not and commonly is not confined to just this one stage of emulsion preparation. 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.

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

The silver bromoiodide high aspect ratio tabular grain emulsions of the present invention are preferably washed to remove soluble salts. Conventional washing procedures, such as those disclosed in Research Disclosure, Vol. 176, Dec. 1978, Paragraph II are contemplated.

In accordance with established practices within the art it is specifically contemplated to blend the high aspect ratio tabular grain emulsions prepared by the process of the present invention with each other or with conventional emulsions to satisfy specific emulsion 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 characteris-

tic curve shape between its toe and shoulder. To accomplish this the emulsions of this invention can be blended with conventional silver halide emulsions, such as those described in Research Disclosure, Item 17643, cited above, Paragraph 1. When a relatively fine grain silver chloride emulsion is blended with the silver bromoiodide emulsions of the present invention, a further increase in the sensitivity—i.e., speed-granularity relationship—of the emulsion can result.

Once silver bromoiodide high aspect ratio tabular grain emulsions have been prepared by the process of the present invention, they can be further modified, coated, exposed, and processed following procedures well known to those skilled in the art.

The emulsions prepared by the present process can be chemically sensitized, as described in Research Disclosure, Item 17643, cited above, Paragraph III. The emulsions can be spectrally sensitized and/or desensitized, as described in Paragraph IV. It is specifically preferred to substantially optimally chemically and spectrally sensitize the emulsions prepared by the present process by the techniques disclosed in Kofron et al, and Maskasky U.S. Patent 4,435,501, cited above.

The photographic emulsions can contain brighteners, antifoggants, stabilizers, scattering or absorbing materials, hardeners, coating aids, plasticizers, lubricants, and matting agents, as described in Item 17643, Paragraphs V, VI, VIII, X, XI, XII, and XVI. Methods of addition and coating and drying procedures can be employed, as described in Paragraphs XIV and XV. Conventional photographic supports can be employed, as described in Paragraph XVII. The photographic elements produced can be black-and-white or, preferably, color photographic elements which form silver images and/or dye images through the selective destruction, formation, or physical removal of dyes, as described in Paragraph VII. Specifically preferred color photographic elements are those which form dye images through the use of color developing agents and dye-forming couplers. To put the photographic elements to use, they can be conventionally exposed, as described in Paragraph XVIII, and they can be conventionally processed, as described in Paragraph XIX.

Examples

The invention can be better appreciated by reference to 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 other-

wise indicated; and the term "M" stands for molar concentration, unless otherwise indicated. All solutions, unless otherwise indicated are aqueous solutions.

Emulsion 1 (Control)

The following is representative of type of silver bromiodide high aspect ratio tabular grain emulsion on which the art is now relying for the highest achievable photographic performance.

To 1.5 liters of a 0.25 percent gelatin solution containing 0.05M sodium bromide at 50 °C, pH 5.8, was added with vigorous stirring 0.12M silver nitrate solution over a 2.0 minute period (consuming 0.55 percent of the total silver used). The temperature was then raised to 70 °C over four minutes and held at 70 °C for a further six minutes. One and one half liters of aqueous gelatin solution (4.3 percent by weight) were added to the reaction vessel. The pBr within the reaction vessel was then adjusted to 1.13 at 70 °C. A halide solution containing sodium bromide (1.89M) plus potassium iodide (0.06M) and a 1.50M silver nitrate solution were added by double jet addition utilizing accelerated flow (7 X increase in flow rates from start to finish) for 40 minutes at pBr 1.13 at 70 °C, consuming 99.45 percent of the total silver used. Approximately 2.2 moles of silver were used to prepare this emulsion.

The resultant silver bromiodide high aspect ratio tabular grain emulsion had an average grain diameter of 2.17 μm , an average tabular grain thickness of 0.08 μm , an average aspect ratio of 27, and a coefficient of variation, based on the total grain population, of 69. Tabular grains accounted for 85% of the total grain projected area.

The quotient of the average aspect ratio divided by coefficient of variation was 0.4. This demonstrates a conventional relationship between tabularity (average aspect ratio) and dispersity (coefficient of variation). It is a significantly worse relationship (lower quotient) than is achieved by the present invention.

Emulsion 2 (Invention)

To 1.5 liters of a 0.25 percent gelatin solution containing 0.05M sodium bromide at 50 °C, pH 5.8, was added with vigorous stirring 4 mL of 3M silver nitrate solution over a 2 second period (consuming 0.55 percent of the total silver used). The temperature was then raised to 70 °C over four minutes and held at 70 °C for a further six minutes. One and one half liters of aqueous gelatin solution (4.3 percent by weight) were added to the reaction

vessel. The pBr within the reaction vessel was then adjusted to 1.78 at 70 °C. A halide solution containing sodium bromide (1.89M) plus potassium iodide (0.06M) and a 1.5M silver nitrate solution were added by double jet addition utilizing accelerated flow (14 X increase in flow rates from start to finish) for 42 minutes at pBr 1.78 at 70 °C, consuming 99.45 percent of the total silver used. Approximately 2.2 moles of silver were used to prepare this emulsion.

The resultant silver bromiodide high aspect ratio tabular grain emulsion had an average grain diameter of 1.78 μm , an average tabular grain thickness of 0.08 μm , an average aspect ratio of 22, and a coefficient of variation, based on the total grain population, of 29. Tabular grains accounted for 85% of the total grain projected area.

The quotient of the average aspect ratio divided by coefficient of variation was 0.76. This demonstrates a significant improvement in the relationship between tabularity (average aspect ratio) and dispersity (coefficient of variation). It is a significantly better relationship (higher quotient) than was achieved using the comparable conventional emulsion preparation technique of control Emulsion 1.

Emulsion 3 (Invention)

To 1.5 liters of a 0.25 percent gelatin solution containing 0.05M sodium bromide at 50 °C, pH 5.8, was added with vigorous stirring 4 mL of 3M silver nitrate solution over a 2 second period (consuming 0.55 percent of the total silver used). The temperature was then raised to 70 °C over four minutes. To the reaction vessel was then added 0.17 millimole of 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane. The reaction vessel was held at 70 °C for a further six minutes. One and one half liters of aqueous gelatin solution (4.3 percent by weight) were added to the reaction vessel. The pBr within the reaction vessel was then adjusted to 1.78 at 70 °C. A halide solution containing sodium bromide (1.89M) plus potassium iodide (0.06M) and a 1.5M silver nitrate solution were added by double jet addition utilizing accelerated flow (14 X increase in flow rates from start to finish) for 42 minutes at pBr 1.78 at 70 °C, consuming 99.45 percent of the total silver used. Approximately 2.2 moles of silver were used to prepare this emulsion.

The resultant silver bromiodide high aspect ratio tabular grain emulsion had an average grain diameter of 2.35 μm , an average tabular grain thickness of 0.12 μm , an average aspect ratio of 20, and a coefficient of variation, based on the total grain population, of 23. Tabular grains accounted for 88% of the total grain projected area.

The quotient of the average aspect ratio divided by coefficient of variation was 0.87. This demonstrates a significant improvement in the relationship between tabularity (average aspect ratio) and dispersity (coefficient of variation). It is a significantly better relationship (higher quotient) than was achieved using the comparable conventional emulsion preparation technique of control Emulsion 1.

Comparing Emulsions 2 and 3, it is apparent that the addition of the thioether ripening agent caused the tabular grains to grow larger in diameter and somewhat thicker by ripening out a higher proportion of smaller grains, reflected in the increased percentage of the total grain projected area accounted for by the tabular grains. While the ripening agent actually lowered the average tabular grain aspect ratio slightly, it reduced the coefficient by a relatively much larger amount, thereby raising the quotient, indicating an overall improved relationship of tabularity and dispersity in the direction of ideal monodispersity.

Emulsion 4 (Control)

This emulsion is neither a conventional emulsion or an example of the invention. It is an in-between emulsion offered to shed light on the question suggested by a comparison of Emulsions 2 and 3 as to whether reliance on the thioether ripening agent without concurrent reliance on accelerated nucleation would produce an emulsion satisfying the tabularity to dispersity requirement of this invention.

To 1.5 liters of a 0.25 percent gelatin solution containing 0.05M sodium bromide at 50°C, pH 5.8, was added with vigorous stirring 0.12M silver nitrate solution over a 2.0 minute period (consuming 0.55 percent of the total silver used). The temperature was then raised to 70°C over four minutes. To the reaction vessel was then added 0.08 millimole of 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane. The reaction vessel was held at 70°C for a further six minutes. One and one half liters of aqueous gelatin solution (4.3 percent by weight) were added to the reaction vessel. The pBr within the reaction vessel was then adjusted to 1.78 at 70°C. A halide solution containing sodium bromide (1.89M) plus potassium iodide (0.06M) and a 1.5M silver nitrate solution were added by double jet addition utilizing accelerated flow (7 X increase in flow rates from start to finish) for 40 minutes at pBr 1.78 at 70°C, consuming 99.45 percent of the total silver used. Approximately 2.2 moles of silver were used to prepare this emulsion.

The resultant silver bromiodide high aspect ratio tabular grain emulsion had an average grain

diameter of 1.77 μm, an average tabular grain thickness of 0.09 μm, an average aspect ratio of 20, and a coefficient of variation of 31. Tabular grains accounted for 88% of the total grain projected area.

The quotient of the average aspect ratio divided by coefficient of variation was 0.65. From this data it appears that the slower nucleation produced a dispersity in the grain nuclei that could not be overcome by subsequent ripening. It appears that the ripening agent ripened out about the same proportion of nontabular grains, but the slower nucleation resulted in a significantly higher dispersity within the tabular grain population.

Emulsion 5 (Invention)

This emulsion is offered to illustrate the formation of a silver bromiodide high aspect ratio tabular grain emulsion according to the invention having a mean grain thickness of less than 0.05 μm, facilitated by the use of gelatin peptizer treated with an oxidizing agent to eliminate methionine.

To an 18 liter stainless steel reaction vessel was added, with vigorous stirring 6.0 liters of 0.125 percent oxidizing agent treated (less than 30 micromoles per gram residual unoxidized methionine) gelatin solution containing 0.04 moles of sodium bromide at 45°C with the pH adjusted to 1.85 using sulfuric acid. To this solution was added 8.0 mL of 1.67M silver nitrate along with 8.0 mL of 1.6M halide solution consisting of 98.5 mole percent sodium bromide and 1.5 mole percent potassium iodide by balanced double jet addition at 120 mL per minute. The temperature was then raised to 60°C over 9 minutes and held for an additional 9 minutes. This was followed by the addition of 100g of the oxidizing agent treated gelatin and a pH adjustment to 5.85 using 2.5M sodium hydroxide. The pBr was then adjusted to 1.75 using a 1.0M sodium bromide for 40 minutes at 12.5 mL per minute with the pBr maintained at 1.75. The solution addition was then stopped for 90 seconds while the pBr was adjusted to 1.55 using the 175M sodium bromide solution. This was followed by a triple jet addition of 1.6M silver nitrate, 0.048M silver iodide Lippmann emulsion suspension, and 1.75M sodium bromide solution. The triple jet addition of the same solutions previously described was then continued with a linearly accelerated flow rate from 12.5 mL per minute to 120 mL per minute. This yielded 6 moles of a silver bromiodide very thin tabular grain emulsion, which was coagulation washed by the procedure of Yutzy et al U.S. Patent 2,614,929.

The resultant silver bromiodide high aspect ratio tabular grain emulsion had an average grain

diameter of 2.9 μm , an average tabular grain thickness of 0.04 μm , an average aspect ratio of 72, and a coefficient of variation, based on the total grain population, of 56.

The quotient of the average aspect ratio divided by coefficient of variation was 1.3. From this data it appears that the reduction in the thickness of the tabular grains resulted in a large increase in projected area that more than offset a modest rise in the coefficient of variation, which was an expected result of increasing the mean grain diameter of the emulsion.

Emulsion 6 (Invention)

Because of the very favorable relationship of tabularity and dispersity achieved by the Emulsion 5, it was possible to substitute a single jet nucleation for the double jet nucleation employed in the preparation of Emulsion 5 while still obtaining a silver bromiodide high aspect ratio tabular grain emulsion having a quotient of average aspect ratio divided by coefficient of variation well in excess of 0.7.

The initial solution before nucleation was prepared as described for Emulsion 5. The balanced double jet nucleation employed for Emulsion 5 was replaced by a single jet nucleation consisting of 8.0 mL of 1.67M silver nitrate solution delivered at approximately 5000 mL per minute. This was immediately followed by a temperature rise, hold time, gelatin addition, pH and pBr adjustments, and an initial constant flow rate triple jet addition that were identical to that of Emulsion 5. The pBr adjustment to 1.55 of Emulsion 5 was replaced with a pBr adjustment to 1.85 using the 1.6M silver nitrate solution. The final ramped flow rate triple jet addition was identical to that of Emulsion 5, except that the pBr was controlled at 1.85.

The resultant silver bromiodide high aspect ratio tabular grain emulsion had an average grain diameter of 2.3 μm , an average tabular grain thickness of 0.045 μm , an average aspect ratio of 51, and a coefficient of variation, based on the total grain population, of 43.

The quotient of the average aspect ratio divided by coefficient of variation was 1.2.

Emulsion 7 (Invention)

This emulsion is offered to illustrate the formation of a silver bromiodide high aspect ratio tabular grain emulsion according to the invention wherein silver iodide was abruptly added as a Lippmann emulsion during grain growth.

To an 18 liter stainless steel reaction vessel

was added with vigorous stirring 6.0 liters of 0.125 percent oxidizing agent treated (less than 30 micro-moles per gram residual unoxidized methionine) gelatin solution containing 0.04 moles of sodium bromide at 4506 with the pH adjusted to 1.85 using sulfuric acid. To this solution was added 8.0 mL of 1.67M silver nitrate along with 8.0 mL of 1.6M halide solution consisting of 98.5 mole percent sodium bromide and 1.5 mole percent potassium iodide by balanced double jet addition at 120 mL per minute. After 60 seconds the pBr was adjusted to 1.73 by the addition of 1.0M sodium bromide. The temperature was then raised to 60°C over 9 minutes and held for an additional 9 minutes. This was followed by the addition of 100g of the oxidizing agent treated gelatin and a pH adjustment to 5.85 using 2.5M sodium hydroxide. The triple jet addition of 1.6M silver nitrate, 0.024M silver iodide Lippmann emulsion suspension, and 1.75M sodium bromide solution was then run at 12.5 mL per minute for 40 minutes with the pBr controlled at 1.83. The triple jet addition was then continued with a linearly accelerated flow rate from 12.5 mL per minute to 120 mL per minute over 35.8 minutes. The addition was then stopped and 0.12 moles of silver iodide Lippmann were added. A double jet addition of 1.6M silver nitrate and 1.75M sodium bromide was then run at 100 mL per minute for 3.65 minutes with pBr controlled at 1.83. This yielded 6 moles of a silver bromiodide very thin tabular grain emulsion, which was coagulation washed by the procedure of Yutzy et al U.S. Patent 2,614,929.

The resultant silver bromiodide high aspect ratio tabular grain emulsion contained over 90 percent tabular grains, had an average grain diameter of 2.85 μm , an average tabular grain thickness of 0.06 μm , an average aspect ratio of 47.5, and a coefficient of variation, based on the total grain population, of 38.

The quotient of the average aspect ratio divided by coefficient of variation was 1.25. From this data it is apparent that the addition of silver iodide during the growth stage of tabular grain formation as a Lippmann emulsion suspension is entirely compatible with obtaining a high quotient of average aspect ratio divided by the coefficient of variation.

Taken as a whole the examples suggest that once the overall strategy for preparing a silver bromiodide high aspect ratio tabular grain emulsion having a favorable relationship of tabularity and dispersity (a high quotient of the average aspect ratio divided by the coefficient of variation) is appreciated from the discussion above in the specification, the desired emulsions can be realized with some freedom in selection of individual preparation parameters, not all of which are of

equal importance. It is therefore apparent that variant procedures will occur to those skilled in the art having access to the teachings of this invention.

The invention has been described in terms of coefficients of variation of grain diameters. Since nontabular grain populations exhibit diameters based on their projected areas that are essentially the same as their thickness, the art has not yet addressed the coefficients of variation for tabular grain emulsions based on variations in tabular grain thicknesses as opposed to variations in tabular grain diameter (the diameter of a circle having the same projected area as the tabular grain). Measurements of tabular grain thickness variation are of necessity somewhat more difficult to generate, since tabular grain thicknesses are much smaller than tabular grain diameters and must be determined indirectly by shadow length measurements of carbon grain replicas. Nevertheless, analysis of this type has been performed, and it has been determined that the emulsion preparation strategies and specific techniques herein disclosed are also effective to reduce variations in tabular grain thicknesses. Although differences in thickness from one tabular grain to the next are in many instances small, even small differences can have a significant impact on varying the surface area to volume ratio of a tabular grain population.

Claims

1. A high aspect ratio tabular grain emulsion comprised of a dispersing medium and silver bromiodide grains, wherein tabular silver bromiodide grains having a thickness of less than $0.3\ \mu\text{m}$ account for greater than 50 percent of the projected area of the total silver bromiodide grain population and have an average aspect ratio of greater than 12, characterized in that the quotient of the average silver bromiodide tabular grain aspect ratio divided by the coefficient of variation of the total silver bromiodide grain population is greater than 0.7.

2. An emulsion according to claim 1 further characterized in that the tabular grains having a thickness of less than $0.3\ \mu\text{m}$ have an average aspect ratio at least 20.

3. An emulsion according to claim 1 or 2 further characterized in that the tabular grains having a thickness of less than $0.3\ \mu\text{m}$ account for greater than 70 percent of the projected area of the total silver bromiodide grain population.

4. An emulsion according to any one of claims 1 to 3 inclusive further characterized in that the tabular grains having a thickness of less than $0.2\ \mu\text{m}$ account for greater than 70 percent of the

projected area of the total silver bromiodide grain population and have an average aspect ratio of greater than 12.

5. An emulsion according to any one of claims 1 to 4 inclusive further characterized in that the quotient of the average silver bromiodide tabular grain aspect ratio divided by the coefficient of variation of the total silver bromiodide grain population is in the range of from greater than 0.7 to 2.0.

6. An emulsion according to claim 5 further characterized in that the quotient is in the range of from 0.8 to 1.5.

7. An emulsion according to any one of claims 1 to 6 inclusive further characterized in that the dispersing medium is a gelatino-peptizer.

8. An emulsion according to claim 7 further characterized in that the gelatino-peptizer contains less than 30 micromoles per gram of methionine.

9. An emulsion according to claim 8 further characterized in that the tabular grains having a thickness of less than $0.07\ \mu\text{m}$ account for greater than 50 percent of the projected area of the total silver bromiodide grain population and have an average aspect ratio in the range of from 20 to 100.

10. An emulsion according to claim 9 further characterized in that the quotient of the average silver bromiodide tabular grain aspect ratio divided by the coefficient of variation of the total silver bromiodide grain population is in the range of from greater than 1.0 to 1.5.