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(54) **High chloride (100) tabular grain emulsions with modified edge structures.**

(57) Photographic emulsions are disclosed in which at least 50 percent of total grain projected area is accounted for by high (>90%) chloride thin (<0.2 μm) tabular grains having {100} major faces each having at least one edge face oriented in an atomic plane differing from that of major faces to improve photographic performance.

FIG. IA

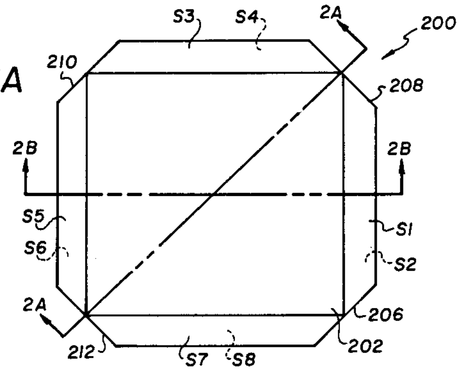
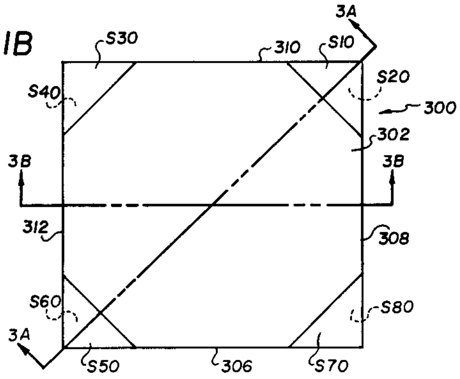


FIG. IB



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The invention relates to radiation sensitive photographic emulsions.

During the 1980's a marked advance took place in silver halide photography based on the discovery that a wide range of photographic advantages, such as improved speed-granularity relationships, increased covering power (both on an absolute basis and as a function of binder hardening), more rapid developability, increased thermal stability, increased separation of native and spectral sensitization imparted imaging speeds, and improved image sharpness in both mono- and multi-emulsion layer formats, can be achieved by employing thin tabular grain emulsions. These advantages are demonstrated in Kofron et al U.S. Patent 4,439,520.

An emulsion is generally understood to be a "thin tabular grain emulsion" when tabular grains having a thickness (t) of less than 0.2 μm account for at least 50 percent of total grain projected area. A grain is easily visually recognized to be a tabular grain when it contains two parallel major faces that are substantially larger than any remaining faces. Quantitatively, a grain with parallel major faces is generally considered to be a tabular grain when its aspect ratio, the ratio of its equivalent circular diameter (ECD) to its thickness (t), is at least 2. The thickness of a tabular grain is the distance between its major faces.

Initially practical interest in tabular grain emulsions centered on applications in camera speed taking films and in indirect radiography (radiographic imaging in which the tabular grain emulsions are imagewise exposed by light emitted from intensifying screens when the screens are exposed to X-radiation). For camera speed films silver iodobromide emulsions have been traditionally preferred and for radiographic films silver bromide emulsions (optionally containing up to about 3 mole percent iodide) have been preferred. The thin tabular grain emulsions that have served these applications have contained tabular grains having opposed {111} major faces. The {111} major faces of the tabular grains exhibit a three-fold symmetry, appearing hexagonal or triangular.

Relatively recently interest has increased in the photographic art in combining the known advantages of thin tabular grain emulsions with the advantages of high chloride grain structures. The term "high chloride" as applied to grain structures and emulsions is herein employed to indicate at least 90 mole percent chloride, based on silver. The advantages that high chloride emulsions offer over those of other halide compositions include lower native blue sensitivity (thereby contributing to the lower color contamination when used as green or red recording emulsion layers), more rapid development rates, and rapid fixing with ecologically preferred sulfite ion fixers.

It was recognized from the outset that quite different emulsion preparation strategies must be practiced to obtain tabular grain emulsions of differing halide content. Although Kofron et al disclosed high chloride tabular grain emulsions, a difficulty that was encountered is that silver chloride exhibits a strong preference for forming grain structures with {100} crystal faces. The high chloride tabular grain emulsions disclosed by Kofron et al exhibit {111} major faces. The use of high chloride {111} tabular grain emulsions has been hampered by the requirement to employ a morphological stabilizer to prevent high chloride {111} tabular grains from reverting to nontabular forms.

Mignot U.S. Patent 4,386,156 (summarized in column 17 of Kofron et al) discloses the preparation of silver bromide tabular grains with {100} major faces. Saito EPO 0 569 971 discloses modified forms of {100} tabular grains containing at least 25 mole percent bromide.

Relatively recently thin, high chloride tabular grain emulsions have been discovered that exhibit {100} crystal faces. By preparing high chloride tabular grains for the first time in an inherently stable crystal form, the complications of morphological stabilizers have been eliminated and remarkable levels of photographic performance have been observed. The sensitivities of these emulsions have approached the sensitivity levels of the more efficient silver iodobromide emulsions. These thin, high chloride {100} tabular grain emulsions are illustrated by Maskasky U.S. Patents 5,264,337, 5,275,930 and 5,292,632; House et al U.S. Patent 5,320,938; Szajewski et al U.S. Patents 5,310,635 and 5,356,764; and Brust et al U.S. Patent 5,314,798.

K. Endo and M. Okaji, "An Empirical Rule to Modify the Crystal Habit of Silver Chloride to Form Tabular Grains in an Emulsion", *J. Photographic Science*, 1988, Vol. 36, (1988), pp. 182-189, set out to produce an empirical rule for selecting materials for use as grain growth modifiers in preparing silver chloride tabular grain emulsions by double-jet precipitation. The rule was tested by adding various ligands, CN^-, SCN^-, I^-, $(S_2O_3)^{-2}$, $(SO_3)^{-3}$ and thiourea (including derivatives) to 3 M sodium chloride solutions at concentrations of 0.001, 0.005, 0.01 and 0.1 M. The 3 M sodium chloride solution was then used with 2 M silver nitrate in double-jet precipitations. Tabular grains having {100} and {111} faces were produced. Based on these investigations Endo et al concluded that to be useful as a grain growth modifier in forming tabular grain high chloride emulsions the first formation constant of the ligand, $\beta_1(L)$, must be more than $\beta_2(Cl^-)$--i.e., $\beta_2(Cl^-)/\beta_1(L)$ must be less than unity (one). In Table 2 Endo et al reported $\beta_2(Cl^-)/\beta_1(L)$ for SCN^- to be 6.3, thereby indicating SCN^- not to be suitable for use as a grain growth modifier. In Figure 7 Endo et al shows a relatively thick silver chloride grain population produced using 0.10 M KSCN.

Maskasky U.S. Patent 5,061,617 discloses employing thiocyanate as a grain growth modifier for the formation of high chloride tabular grains having {111} major faces.

In one aspect this invention is directed to a radiation sensitive emulsion containing a silver halide grain population comprised of at least 90 mole percent chloride, based on silver, wherein at least 50 percent of the total grain population projected area is accounted for by tabular grains (1) bounded by {100} major faces having adjacent edge ratios of less than 10 and (2) having a thickness of less than 0.2 µm; characterized in that each of the tabular grains accounting for at least 50 percent of the total grain projected area (3) contains at least one crystal face that lies in an atomic plane differing from that of the major faces and (4) exhibits a lower grain volume than a tabular grain of the same length, width and thickness bounded entirely by crystal faces lying in {100} atomic planes.

By providing the tabular grains with at least one edge that lies in an atomic plane different from that of the {100} major faces, a different surface pattern of Ag^+ and Cl^- ions are provided as compared to the major faces of the grains, and the photographic utility of the grains is enhanced. Whereas the major faces of the tabular grains lie in {100} atomic planes, from one to twelve edge surfaces of the grains lie in one or more other atomic planes--that is, non-{100} crystal planes. This allows different grain performance enhancing compounds (e.g., spectral sensitizing dyes, chemical sensitizers, antifoggants and stabilizers) to be used in combination selected on the basis of different preferred crystal face affinities. This reduces competition between these compounds for surface sites. For example, by reducing competition between chemical sensitizers and spectral sensitizing dyes, reduced dye desensitization can be achieved. As another example of photographic benefits, dye displacement by antifoggants and stabilizers can be minimized.

Brief Description of the Drawings

Figure 1A is a view normal to a {100} major face of an ideal thin tabular grain satisfying the requirements of the invention having edge crystal faces lying in {110} atomic planes;

Figure 1B is a view normal to a {100} major face of an ideal thin tabular grain of an alternate form satisfying the requirements of the invention having edge crystal faces lying in {111} atomic planes;

Figures 2A and 2B are sectional views taken along section lines 2A-2A and 2B-2B, respectively, in Figure 1A;

Figures 3A and 3B are sectional views taken along section lines 3A-3A and 3B-3B, respectively, in Figure 1B;

Figure 4 is an isometric view of a conventional {100} tabular grain; and

Figure 5 is a shadowed electron micrograph of a tabular grain emulsion satisfying the requirements of the invention.

In Figure 4 a conventional {100} tabular grain **100** is illustrated. The tabular grain has an upper major face **102** and a parallel lower major face **104**. In addition the grain has four edge faces **106**, **108**, **110** and **112** that are oriented perpendicular to the major faces. Each of the edge faces are oriented either parallel to or perpendicular to another edge face. Each of the six faces **102**, **104**, **106**, **108**, **110** and **112** lie in a {100} atomic plane.

In Figures 1A, 2A and 2B a tabular grain **200** is shown which represents one ideal form that the tabular grains in the emulsions of the invention can take. The tabular grain is in part bounded by parallel {100} atomic planes forming major faces **202** and **204**. In addition the tabular grain has eight sloping edge faces, with sloping faces **S1**, **S3**, **S5** and **S7** intersecting the upper {100} major face **202** and sloping faces **S2**, **S4**, **S6** and **S8** intersecting the lower {100} major face **204**. Four additional edge faces **206**, **208**, **210** and **212** are oriented perpendicular to the {100} major faces. By comparing the orientations of the edge faces of grain **200** with the orientations of the edge faces of grain **100**, it is apparent that none of the edge faces of the grain **200** lie in a {100} atomic plane. In grain **200** each of the edge faces lie in [110] atomic planes.

An alternate ideal form of a tabular grain satisfying the requirements of the emulsions of the invention is shown Figures 1B, 3A and 3B. The tabular grain **300** is in part bounded by parallel {100} major faces **302** and **304**. In addition the tabular grain has four edge faces **306**, **308**, **310** and **312** that are oriented with respect to the major faces similarly as the edge faces in tabular grain **100**. That is, these four edge faces are {100} crystal faces. In addition the tabular grain **300** has eight identical sloping edge faces, with sloping edge faces **S10**, **S30**, **S50** and **S70** intersecting the upper major face **302** of the grain and sloping edge faces **S20**, **S40**, **S60** and **S80** intersecting the lower major face of the grain. The sloping edge faces lie in {111} atomic planes.

A difference between {100} tabular grain **100** and the ideal tabular grains **200** and **300** satisfying the requirements of the invention is that the latter exhibit a lower grain volume than tabular grains bounded entirely by {100} crystal faces of the same length, width and thickness. The non-{100} edges of the grains **200** and **300** give the appearance of {100} tabular grains with one or more corners removed. Hence, a name that has been applied to these grains is "cut corner" grains (although, in reality, the corners are not cut away, but simply never formed). An advantage of this is that the tabular grains **200** and **300** require less silver to provide the same projected area for light capture than the tabular grains **100**. Another distinguishing feature of the tabular grains **200** and **300** is common to all tabular grains satisfying the requirements of the invention is that the non-{100} crystal faces do not protrude above the plane of the nearest {100} major face, again contributing to reduced grain volume, based on displacement dimensions.

The emulsions of the invention are similar to conventional thin, high chloride tabular grain emulsions in that at least 50 percent, preferably at least 70 percent and optimally at least 90 percent of total grain projected area is accounted for by tabular grains having {100} major faces. Whereas the tabular grains **100**, **200** and **300** are shown to have major faces of approximately equal length and width, rectangular major faces (with clearly unequal lengths and widths) are common. Therefore, to distinguish the tabular grains from more rod-like grains, the length to width ratio of the grains must be less than 10 and is preferably less than 5 and optimally less than 2.

The tabular grains accounting for at least 50 percent of total grain projected area have a thickness of less than 0.2 μm. In fact, the tabular grains can have any conventional lower thickness desired. For example, as demonstrated in the Examples below, the tabular grains can be ultrathin--that is, exhibit a mean thickness of less than 0.07 μm.

The tabular grains accounting for at least 50 percent of total grain projected area preferably have a mean aspect ratio of greater than 8 and most preferably at least 12. Since the tabular grain structures satisfying the edge requirements of the invention can be grown in the same thickness and ECD ranges as conventional thin {100} tabular grain emulsions, it is apparent that similar mean aspect ratios can be realized.

The tabular grains contain at least 90 mole percent chloride, based on total silver. The remaining halide, if any, can be any convenient combination of bromide and/or iodide. Silver chloride emulsions, those lacking any intentional inclusion of bromide and/or iodide, are specifically contemplated. As demonstrated in the Examples below certain techniques for forming the tabular grain structures of the invention rely upon the inclusion of iodide in the grains. Thus, in one specific, preferred form the tabular grains can consist essentially of silver iodochloride. Optimum iodide concentrations vary, depending upon the photographic application. For example, camera speed films can accommodate iodide concentrations of up to 10 mole percent. For rapid access processing in radiography iodide levels are typically chosen to be less than 3 mole percent, based on silver. In color print emulsions iodide levels are typically maintained at less than 1 mole percent, based on silver. All of these identified photographic applications can accept emulsions containing up to 10 mole percent bromide.

A common distinction between each of the emulsions of the invention and otherwise similar conventional emulsions is that the {100} tabular grains accounting for at least 50 (preferably at least 70 and optimally at least 90) percent of total grain projected area contain non-{100} edge structures.

The ideal tabular grain structure **200** is shown with twelve equal {110} edge faces while the ideal grain structure **300** is shown with eight identical {111} edge faces. These grains are stated to be ideal, since achieving emulsion precipitations with minimal random grain variance affords maximum control over photographic performance. In ideal emulsions the edges of the tabular grains accounting for at least 50 percent of total grain projected area are similarly (equivalently) modified to a non-{100} form.

Some preparation techniques lend themselves to forming ideal grain structures with little grain to grain variance (i.e., monodispersity) within a wider range of conditions than others. Grain variances can be reduced by assuring the uniform availability of reactants. This is more easily accomplished in smaller scale precipitations. In some precipitations in which ideal levels of reactant uniformity are not conveniently realized (e.g., larger scale precipitations), the corners of the tabular grains are non-equivalently modified. That is, the non-{100} crystal face or faces adjacent one corner may be larger than another. Further, one or more corners may be so minimally modified that it is difficult to ascertain whether the grain corner has a non-{100} crystal face or merely rounded by ripening.

Significant photographic advantages can be realized when the tabular grains with {100} major faces accounting for at least 50 percent of total grain projected area contain at least one crystal face lying in a different atomic plane than the {100} major faces. All of the grains produced in precipitation of a high chloride emulsion exhibit a face centered cubic crystal lattice structure, regardless of whether the grains are tabular or nontabular. Further, this is independent of the atomic planes in which the grain surfaces lie.

However, it is important to note that the spatial pattern of Ag$^+$ and Cl$^-$ at the grain surface differs markedly, depending upon the atomic plane in which the grain surface lies. Maskasky U.S. Patent 4,643,966 pictorially illustrates Ag$^+$ and Br$^-$ patterns in {100}, {110}, {111} and four higher index, less common crystal planes. The patterns shown by Maskasky are also formed by AgCl, except that the Cl$^-$ is smaller than the Br$^-$.

The Ag$^+$ and Cl$^-$ pattern in a {100} atomic plane is schematically shown below:

```
Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl
Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag
Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl
Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag
Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl
Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag
Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl
Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag  Cl  Ag
```

The Ag$^+$ and Cl$^-$ pattern in a {110} atomic plane is schematically shown below:

```
  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl
  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl
  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl
  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl  Cl
```

Within the grain {111} atomic planes consist of all Cl$^-$ or all Ag$^+$ in an alternating sequence. Since photographic emulsions contain a stoichiometric excess of halide ions, the surface is believed to be formed of a complete layer of Ag$^+$ onto which is superimposed a complete or incomplete layer of Cl$^-$. The outermost Ag$^+$ {111} crystal plane exhibits the following configuration:

```
  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag  Ag
```

When the outermost Cl {111} atomic plane begins to form on the outermost Ag {111} atomic plane, each Cl$^-$ is located equidistant from three Ag$^+$ ions in the underlying {111} crystal plane. When the Cl$^-$ {111} atomic plane is entirely formed, the Cl$^-$ ions are distributed in the same pattern shown above for the Ag$^+$

ions.

From the foregoing it is apparent that each different atomic plane lying at the surface of the tabular grains of the invention presents a markedly different pattern of cations and anions. Compounds that adsorb to or react with the grain surface to provide photographically useful properties select an atomic plane for interaction based on ionic and steric compatibility.

Although ideal grain structures are illustrated above in terms of non-{100} grain faces lying in {110} or {111} atomic planes, it is appreciated that the non-{100} grain faces can alternatively lie in other atomic planes. Maskasky U.S. Patent 4,643,966, here incorporated by reference, discloses silver halide grain structures bounded by {100}, {110}, {111}, {hhl}, [hk0], {hll} and {hkl} atomic planes, where h, k and l are independently in each occurrence unlike integers greater than zero, where h is greater than l and k, when present, is less than h and greater than l. Although there is no theoretical limit on the maximum value of the integer h, it is in practice usually 5 or less. After a {100} tabular grain emulsion has been precipitated as a host, precipitation techniques selected from among those taught by Maskasky can be employed for completing grain growth, resulting in the emergence of one or more non-{100} crystal faces on the grains.

The emulsions of the invention can be prepared by modifying the preparation of conventional thin, high chloride {100} tabular grain emulsions. That is, conventional {100} tabular grains of the type shown in Figure 3 are first precipitated. Techniques for precipitating an initial thin, high aspect ratio, high chloride {100} tabular grain emulsions are illustrated by Maskasky U.S. Patents 5,264,337, 5,292,930 and 5,292,632; House et al U.S. Patent 5,320,938; Szajewski et al U.S. Patents 5,310,635 and 5,356,764; and Brust et al U.S. Patent 5,314,798; cited above and here incorporated by reference. From 50 to 98 percent, preferably 85 to 95 percent, of the total silver forming the emulsion of the invention is precipitated under these conventional conditions of precipitation. Thereafter, the conditions of precipitation are modified to provide the non-{100} crystal faces while completing grain growth.

In one preferred form of the invention the non-{100} crystal faces are formed while increasing the iodide concentration during precipitation to a level of at least 5 (preferably at least 7) mole percent, based on the silver being concurrently introduced. The iodide can be conveniently added as a silver iodide Lippmann emulsion or as a soluble salt (e.g., KI). The iodide ion concentration level can be increased up to the saturation level of iodide ion in silver chloride. Increasing iodide concentrations above their saturation level in silver chloride runs the risk of precipitating a separate silver iodide phase. Maskasky U.S. Patent 5,288,603, here incorporated by reference, discusses iodide saturation levels in silver chloride and silver bromochloride. The presence of iodide during precipitation in combination with other precipitation parameters results in tabular grain emulsions satisfying the requirements of the invention. Specific illustrations of how iodide incorporation in combination with other precipitation parameters can be utilized to provide tabular grain emulsions satisfying the requirements of the invention are provided in the Examples below. When iodide is relied upon to provide non-{100} crystal faces, the tabular grains can contain as little as 0.1 mole percent iodide, based on total silver, but it is preferred that the grains contain at least about 0.5 mole percent iodide. Tabular grains containing up to 10 mole percent iodide can be prepared using iodide to provide non-{100} edge faces. This preparation approach can be practiced in the presence or absence of bromide. The sum of iodide and bromide can range up to 10 mole percent, based on total silver.

A distinct advantage of employing iodide to provide non-{100} crystal faces is that the inclusion of iodide in the grain structure facilitates latent image formation and can result in realizing increased levels of photographic sensitivity. Further, since the iodide ions are incorporated in the crystal structure, they do not compete with other photographic addenda for adsorption sites on the surfaces the tabular grains.

An alternative to employing iodide for the formation of non-{100} grain faces of the invention is the use of thiocyanate. By using thiocyanate to form the non-{100} grain faces it is possible to precipitate emulsions according to the invention that contain no significant levels of iodide. The thiocyanate can be introduced into the reaction vessel in the form of an alkali, alkaline earth or ammonium salt. Typical thiocyanate concentrations range from 0.2 to 10 (preferably 0.5 to 5) mole percent, based on silver concurrently introduced. Since silver thiocyanate is less soluble than silver chloride, thiocyanate is believed to be incorporated into the grains. As shown in Figure 5 grains prepared in the presence of thiocyanate during the later stages of precipitation generally exhibit at least one crystal face that is readily recognized not to satisfy the permissible orientations of a {100} atomic plane and hence to be a non-{100} crystal face. The specific techniques for forming the tabular grain emulsions of the invention employing thiocyanate are demonstrated in the Examples below. It is recognized that, instead of selecting thiocyanate or iodide to produce non-{100} grain edges, it is possible to employ both in combination.

In still another alternative form of the invention selected organic compounds can be employed for producing {100} tabular grains with non-{100} crystal faces. In the Examples below 4,5,6-triaminopyrimidine and 2,4,6-triiodophenol, known grain growth modifiers for producing {111} grain faces, and 1-(3-acetamidophenyl)-5-mercaptotetrazole, a known grain growth modifier for the formation of {110} grain faces, are demonstrated to be successful in producing non-{111} edge faces on high chloride {100} tabular grains.

It is noted that 4,5,6-triaminopyrimidine is an example of a formula defined family of {111} growth modifiers disclosed in Maskasky U.S. Patent 5,185,239, the disclosure of which is here incorporated by reference. Specifically disclosed compounds include, in addition to 4,5,6-triaminopyrimidine, 5,6-diamino-4-(N-methylaminopyrimidine, 4,5,6-tri(N-methylamino)pyrimidine, 4,6-diamino-5-(N,N-dimethylamino)-pyrimidine and 4,6-diamino-5-(N-hexylamino)pyrimidine. Similar utility is contemplated for various forms of 7-azaindole grain growth modifiers disclosed in Maskasky U.S. Patent 5,178,997, the disclosure of which is here incorporated by reference. In addition to 7-azaindole, specifically disclosed compounds include 4,7-diazaindole, 5,7-diazaindole, 6,7-diazaindole, purine, 4-azabenzimidazole, 4,7-diazabenzimidazole, 4-azabenzotriazole, 4,7-diazazbenzotriazole and 1,2,5,7-tetraazaindene.

Similarly, 2,4,6-triiodophenol is an example of a family of polyiodophenol {111} grain growth modifiers disclosed in Maskasky U.S. Serial No. 281,283, filed July 27, 1994, now allowed and here incorporated by reference. In addition to 2,4,6-triiodophenol, specifically disclosed compounds include 2,6-diiodophenol, 2,6-diiodo-4-nitrophenol, 2,6-diiodo-4-methylphenol, 4-allyl-2,6-diiodophenol, 4-cyclohexyl-2,6-diiodophenol, 2,6-diiodo-4-phenylphenol, 4,6-diiodo-2-acetophenone, 4,6-diiodothymol, 4,6-diiodocarvacrol, 3,5-diiodo-L-tyrosine, 3',3",5',5"-tetraiodophenolphthalein, erythrosin and rose bengal. Structurally similar to the polyiodophenol grain growth modifiers are the iodoquinoline {111} grain growth modifiers disclosed in Maskasky U.S. Serial No. 281,500, filed July 27, 1994, now allowed and here incorporated by reference. Specific examples of iodoquinoline grain growth modifiers are 5-chloro-8-hydroxy-7-iodoquinoline, 8-hydroxy-7-iodo-2-methylquinoline, 4-ethyl-8-hydroxy-7-iodoquinoline, 5-bromo-8-hydroxyiodoquinoline, 5,7-diiodo-8-hydroxyquinone, 8-hydroxy-7-iodo-5-quinolinesulfonic acid, 8-hydroxy-7-iodo-5-quinolinecarboxylic acid, 8-hydroxy-7-iodo-5-iodomethylquinoline, 8-hydroxy-7-iodo-5-trichloromethylquinoline, α-(8-hydroxy-7-iodoquinoline)acetic acid, 7-cyano-8-hydroxy-5-iodoquinoline and 8-hydroxy-7-iodo-5-isocyanatoquinoline. Similar utility is contemplated for similar {111} grain growth modifiers, such as the various forms of 5-iodobenzoxazolium compounds disclosed in Maskasky U.S. Patent 5,298,387, the disclosure of which is here incorporated by reference, and the various forms of benzimidazolium compounds disclosed in Maskasky U.S. Patent 5,298,388, the disclosure of which is here incorporated by reference.

The utility of 1-(3-acetamidophenyl)-5-mercaptotetrazole (APMT) as a grain growth modifier in the practice of the invention is highly advantageous, since AMPT is a widely used and preferred antifoggant and stabilizer for high chloride photographic emulsions. Thus, the grain growth modifier is capable of serving a second photographic function after the grains have been formed.

AMPT is an example of thionamide compounds known to be useful {110} grain growth modifiers. The common feature of these compounds is a thioamide, -NH-C(S)-, group. Thioamide compounds and their utility as grain growth modifiers are disclosed in Maskasky, "The Seven Different Kinds of Crystal Forms of Photographic Silver Halides, ***Journal of Imaging Science,*** No. 6, Nov./Dec. 1986, pp. 247-254.

In the preparation of high chloride {111} tabular grain emulsions the use of adsorbed grain growth modifiers to create and preserve the {111} grain faces is disadvantageous, since at least both of the major faces of each {111} tabular grain has a grain growth modifier adsorbed to it. The effective grain growth modifiers identified in this patent application are adsorbed to the faces of the {100} tabular grains that lie in non-{100} atomic planes. That is, non-{100} edge faces emerge because these are the crystal faces for which the effective grain growth modifiers show an adsorption preference. Thus, the grain growth modifiers show a relatively lower affinity for the {100} major faces of the tabular grains, leaving the {100} major faces free to accept other photographic addenda. Hence, high chloride emulsions containing {100} tabular grain emulsions prepared with non-{100} grain edges by employing an adsorbed grain growth modifier exhibit a significant advantage over {111} tabular grain emulsion even when the two emulsions are prepared using identical grain growth modifiers.

The thionamide compound 2-mercaptopyridine and a related compound 5-carboxy-4-hydroxy-6-methyl-2-methylthio-1,3,3a,7-tetraazaindene are demonstrated in the Examples below to have failed to produce tabular grains with grain surfaces lying in different atomic planes. A similar failure is reported in the Examples below for adenine, the original and most widely cited grain growth modifier for precipitating high chloride {111} tabular grains, illustrated by Maskasky U.S. Patents 4,400,463 and 4,713,323, Jones et al U.S. Patent 5,176,991, Maskasky U.S. Patent 5,183,239 and Verbeek EPO 0 481 133. Unfortunately, instead of producing non-{100} crystal faces selectively at the edges of the grains, these known grain growth modifiers have caused silver chloride to be deposited over the entire exterior face of the grains, producing grain surface ruffling of the type disclosed by Maskasky U.S. Patent 4,643,966 in addition to sloping edge protrusions. Thus, the objective of obtaining tabular grains with faces having differing crystal plane orientations has not been realized.

It is believed that the success reported in the Examples in achieving non-{100} edge facets while preserving {100} major grain faces has resulted from achieving a balance in which silver and chloride precipitation is occurring nearer to equilibrium. That is in the reaction

$$Ag^+ + Cl^- \leftrightarrow AgCl$$

the driving force is to the right, but is sufficiently limited that the higher reactive energy of the grain substrate at the edge regions as compared to the major faces allows the edge regions to act as preferred reception sites for deposition.

Apart from emulsion grain features specifically discussed, the emulsions of the invention and the photographic elements in which they can be employed can include the features of {100} tabular grain emulsions disclosed by Maskasky U.S. Patents 5,292,930 and 5,292,632; House et al U.S. Patent 5,320,938; Szajewski et al U.S. Patents 5,310,635 and 5,356,764; and Brust et al U.S. Patent 5,314,798; cited above and here incorporated by reference. The features of photographic elements in which the emulsions of the invention can be employed and the use of such photographic elements are further described in *Research Disclosure*, Vol. 365, Sept. 1994, Item 36544. *Research Disclosure* is published by Kenneth Mason Publications, Ltd., Dudley House, 12 North St., Emsworth, Hampshire P010 7DQ, England.

Examples

The invention can be appreciated by reference to the following specific Examples. The acronym DW is employed to indicate distilled water. Speed is reported in relative log units (i.e., 30 units = 0.3 log E, where E is exposure in lux-seconds).

Examples 1 to 4

These examples demonstrate the effectiveness of thiocyanate to produce non-{100} grain faces on high chloride tabular grains bounded by {100} major faces.

Example 1

Emulsion A

(control)

Six solutions were prepared as follows:

Solution 1	
Gelatin (bone)	75 g
NaCl	2.88 g
KI	0.44 g
DW	4300 g

Solution 2	
NaCl	397.4 g
DW to total volume	1700 mL

Solution 3	
NaCl	4.3 g
DW	6500 g

Solution 4	
$AgNO_3$	1155 g
D. W. to total volume	1700 mL

Solution 5	
Gelatin (phthalated)	200 g
DW	1500 g

Solution 6	
Gelatin (bone)	130 g
DW	1500 g

Solution 1 was charged into a reaction vessel equipped with a stirrer. The pH was adjusted to 6.5, and the temperature was raised to 55 ° C. While vigorously stirring the contents of the reaction vessel, Solution 2 and Solution 4 were added at 45 mL/min for one minute. Solution 3 was then added to the mixture. Mercurous chloride antifoggant in the amount of 0.066 mg/Ag mole was then added to the portion Solution 4 that had not been added to the reaction vessel. The pH was adjusted to 6.5, the pCl was adjusted to 1.91 while maintaining the pH at 6.5. The mixture was held for five minutes. Following this hold, Solution 2 and Solution 4 were each added simultaneously at linearly accelerated rates of from 15 mL/min to 37 mL/min in 56 minutes with the pCl maintained at 1.91. The mixture was then cooled to 40 ° C, and Solution 5 was added with stirring, which continued for 5 minutes. The pH was then adjusted to 3.8, and the gel was allowed to settle. At the same time the temperature was dropped to 15 ° C before decanting the liquid layer. The depleted volume was restored with DW. The pH was adjusted to 4.5, and the mixture held at 40 ° C 20 minutes before the pH was adjusted to 3.8. The settling and decanting steps repeated. Solution 6 was added, and the pH and pCl were adjusted to 5.6 and 1.6, respectively.

Examination of the grain structure revealed that >70 percent of total grain projected area was accounted for by {100} tabular grains. The tabular grains lacked any identifiable non-{100} faces. The {100} tabular grains had a mean thickness of 0.14 μm and a mean equivalent circular diameter (ECD) of 1.4 μm.

Emulsion B

(example)

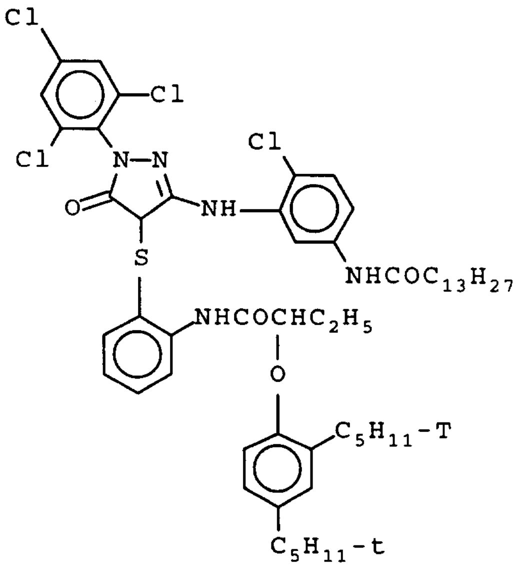
Emulsion B was prepared like Emulsion A, except that the precipitation was interrupted after 80% of total silver had been introduced in the reaction vessel to allow the addition of a solution of 3.0 g of NaSCN in 20 cc of DW to the reaction vessel over 2 min.

Examination of the grain structure revealed that >70 percent of total grain projected area was accounted for by tabular grains with {100} major faces containing at least one identifiable non-{100} edge face. The tabular grains had a mean thickness of 0.13 μm and a mean equivalent circular diameter (ECD) of 1.4 μm.

Finishing, Coating and Sensitometry

Emulsions A and B were finished by adding 1 mole % NaBr, based on silver, followed by holding for 5 minutes, adding spectral sensitizing dye anhydro-9-ethyl-5,5'-diphenyl-3,3'-di(3-sulfobutyl)oxacarbocyanine hydroxide, monosodium salt (SS-1) at 0.7 mmole/Ag mole followed by holding for 10 minutes, adding $Na_2S_2O_3 \cdot 5H_2O$ at 2 mg/Ag mole and $KAuCl_4$ at 1 mg/Ag mole followed by heating for 10 minutes at 60 ° C, cooling to 40 ° C and adding 1-(3-acetamidophenyl)-5-mercaptotetrazole (APMT) at 100 mg/mole after the heating step. Note that since the APMT is not added until after the emulsion grains have been formed, the APMT is incapable of acting as a grain growth modifier.

The finished emulsions were coated on a photographic film support at 5.38 mg Ag/dm^2 with a magenta dye forming coupler MC-1 at 4.84 mg/dm^2. The coatings were overcoated with gel and hardened.



MC-1

The coatings were given an exposure of 1/50 sec through a graduated test object with simulated daylight and photographically processed for 2′ 15″ in the Kodak Flexicolor ™ C-41 color negative process, described in the *British Journal of Photography Annual* of 1988, pp. 196-198.

The sensitometric results are summarized in Table I. Speed was measured at the intersection of the extrapolation mid-scale contrast (γ) to minimum density (Dmin).

Table I

Emulsion	SCN	Speed	γ
A	undoped	200	1.62
B	1.0 mole %	204	0.87

Emulsion B satisfying the requirements of the invention exhibited significantly reduced contrast and nominally increased speed compared to the control emulsion.

Example 2

Emulsion C

(control)

Six solutions were prepared as follows:

Solution 1	
Gelatin (bone)	52 g
NaCl	0.96 g
KI	0.18 g
DW	2850 g

Solution 2	
NaCl	257.1 g
DW to total volume	1100 mL

Solution 3	
NaCl	2.1 g
DW	6500 g

Solution 4	
$AgNO_3$	747.4 g
DW to total volume	1100 mL

Solution 5	
Gelatin (phthalated)	133 g
DW	500 g

Solution 6	
Gelatin (bone)	87 g
DW	500 g

Solution 1 was charged into a reaction vessel equipped with a stirrer. The pH was adjusted to 6.5, and the temperature was raised to 55 ° C. While vigorously stirring the contents of the reaction vessel, Solution 2 and Solution 4 were added at 130 mL/min for one half minute. Solution 3 was then added to the mixture. The temperature of the reaction vessel was raised to 62 ° C, the pH Was adjusted to 6.5, and the pCl was adjusted to 1.91 while the pH was maintained at 6.5. The mixture was held for five minutes. Following this hold, Solution 2 and Solution 4 were added simultaneously each at a linearly accelerated rates of from 10 mL/min to 24 mL/min in 56 minutes with the pCl maintained at 1.91. The mixture was then cooled to 40 ° C, and Solution 5 was added and stirred for 5 minutes. The pH was then adjusted to 3.8, and the gel was allowed to settle. At the same time the temperature was dropped to 15 ° C before decanting the liquid layer. The depleted volume was restored with DW. The pH was adjusted to 4.5, and the mixture was held at 40 ° C for 20 min before the pH was adjusted to 3.8 and the settling and decanting steps were repeated. Solution 6 was added, and the pH and pCl were adjusted to 5.6 and 1.6, respectively.

Examination of the grain structure revealed that >80 percent of total grain projected area was accounted for by {100} tabular grains. The tabular grains lacked any identifiable non-{100} faces. The {100} tabular grains had a mean thickness of 0.14 µm and a mean equivalent circular diameter (ECD) of 1.3 µm.

Emulsion D

(example)

Emulsion D was prepared like Emulsion C, except that the precipitation was interrupted after 80% of the total silver had been introduced to allow the addition of a solution of 1.6 g of NaSCN in 20 cc of DW to the reaction vessel over 2 min.

Examination of the grain structure revealed that >80 percent of total grain projected area was accounted for by tabular grains with {100} major faces containing at least one identifiable non-{100} edge face. The tabular grains had a mean thickness of 0.14 µm, a mean equivalent circular diameter (ECD) of 1.4 µm.

Example 3

Emulsion E

(control)

Six solutions were prepared as follows:

Solution 1	
Gelatin (bone)	25 g
NaCl	0.96 g
KI	0.18 g
DW	2850 g

Solution 2	
NaCl	257.1 g
DW to total volume	1100 mL

Solution 3	
NaCl	2.1 g
DW	6500 g

Solution 4	
$AgNO_3$	747.4 g
DW to total volume	1100 mL

Solution 5	
Gelatin (phthalated)	133 g
DW	500 g

Solution 6	
Gelatin (bone)	87 g
DW	500 g

Solution 1 was charged into a reaction vessel equipped with a stirrer. The pH was adjusted to 6.5, and the temperature was raised to 55 ° C. While vigorously stirring the contents of the reaction vessel, Solution 2 and Solution 4 were added at 130 ml/min for one half minute. Solution 3 was then added to the mixture. Mercurous chloride antifoggant in the amount of 0.11 mg/Ag mole was then added to the portion Solution 4 that had not been added to the reaction vessel. The temperature of the reaction vessel was raised to 62 ° C, the pH adjusted to 6.5, and the pCl was adjusted to 1.91 while the pH was maintained at 6.5. The mixture was held for five minutes. Following this hold, Solution 2 and Solution 4 were added simultaneously each at a linearly accelerated rates of from 10 mL/min to 24 mL/min in 56 minutes with the pCl maintained at 1.91. The mixture was then cooled to 40 ° C, Solution 5 was added, and the contents of the reaction vessel were stirred for 5 minutes. The pH was then adjusted to 3.8, and the gel was allowed to settle. At the same time the temperature was dropped to 15°C before decanting the liquid layer. The depleted volume was restored with DW. The pH was adjusted to 4.5, and the mixture was held at 40°C for 20 minutes before the pH was adjusted to 3.8. The settling and decanting steps repeated. Solution 6 was added, and the pH and pCl adjusted to 5.6 and 1.6, respectively.

Examination of the grain structure revealed that >70 percent of total grain projected area was accounted for by {100} tabular grains. The tabular grains lacked any identifiable non-{100} faces. The {100} tabular grains had a mean thickness of 0.14 µm and a mean equivalent circular diameter (ECD) of 1.5 µm.

Emulsion F

(example)

Emulsion F was prepared like Emulsion E, except that the precipitation was interrupted after 80% of the total silver had been introduced to allow a solution of 1.6 g of NaSCN in 20 cc of DW to be added to the reaction vessel over 2 min.

Examination of the grain structure revealed that >65 percent of total grain projected area was accounted for by tabular grains with {100} major faces containing at least one identifiable non-{100} edge face. The tabular grains had a mean thickness of 0.14 µm and a mean equivalent circular diameter (ECD) of 1.4 µm.

Emulsion G

(example)

Emulsion G was prepared like Emulsion E, except that the precipitation was interrupted after 60% of the total silver had been introduced to allow the addition of a solution of 3.24 g of NaSCN in 20 cc of DW to the reaction vessel over 2 min.

Examination of the grain structure revealed that >60 percent of total grain projected area was accounted for by tabular grains with {100} major faces containing at least one identifiable non-{100} edge face. The tabular grains had a mean thickness of 0.13 µm and a mean equivalent circular diameter (ECD) of 1.38 µm. A shadowed electron micrograph of grain replicas is shown in Figure 5.

Emulsion H

(example)

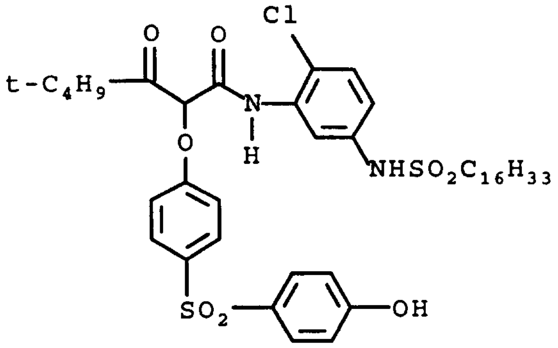
Emulsion H was prepared like Emulsion E, except that the precipitation was interrupted after 40% of total silver had been introduced to all the addition of a solution of 3.24 g of NaSCN in 20 cc of DW to the reaction vessel over 2 min.

Examination of the grain structure revealed that >70 percent of total grain projected area was accounted for by tabular grains with {100} major faces containing at least one identifiable non-{100} edge face. The tabular grains had a mean thickness of 0.13 µm and a mean equivalent circular diameter (ECD) of 1.09 µm.

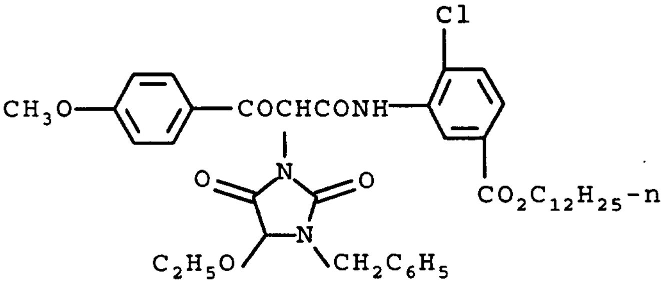
Finishing, Coating and Sensitometry

Emulsions E and F were finished with 4,4'-diphenyldisulfidediacetanilide antifoggant at 6 and 4 mg/Ag mole respectively. Sodium bromide in the amount of 0.25 mole %, based on silver was introduced followed by holding for 5 minutes. The spectral sensitizing dye anhydro 3'-methyl-4'-phenyl-1-(3-sulfopropyl)-naphtho[1,2-d]thiazolothiazolocyanine hydroxide (SS-2) was added 0.8 mmole/Ag mole, followed by holding for 10 minutes. The emulsions were then chemically sensitized by adding $Na_2S_2O_3 \cdot 5H_2O$ at 2.8 mg/Ag mole and $KAuCl_4$ at 1.4 mg/Ag mole and heating for 10 minutes at 60°C. AMPT antifoggant at 100 mg/Ag mole was added after the heating step.

The finished emulsions were each coated at 9.65 mg Ag/dm^2 with a combination of yellow dye-forming couplers YC-1 and YC-2 at 1:1 molar at a combined overage of 9.65 mg/dm^2. The coatings were overcoated with gel and hardened.



YC-1



YC-2

The coatings were given an exposure of 1/50 sec through a graduated test object with simulated daylight and photographically processed for 3′ 15″ in the Kodak Flexicolor ™ C-41 color negative process.

The sensitometric results are summarized in Table II. Speed measurements are the same as that reported in Table I.

Table II

Emulsion	SCN Dump	fog	speed	γ
E	undoped	0.46	200	2.17
F	0.5 mole %	0.28	195	1.91

Emulsion F satisfying the requirements of the invention exhibited significantly reduced fog and contrast compared to the control emulsion. Speed was also slightly reduced.

Example 4

Emulsion J

(control)

Six solutions were prepared as follows:

Solution	
Gelatin (bone)	25 g
NaCl	0.96 g
KI	0.18 g
DW	2824 g

Solution 2	
NaCl DW to total volume	284 g 1215 mL

Solution 3	
NaCl DW	2.1 g 6488 g

Solution 4	
$AgNO_3$ DW to total volume	756.6 g 1069 mL

Solution 5	
Gelatin (phthalated) DW	133 g 500 g

Solution 6	
DW Gelatin (bone)	500 g 90 g

Solution 1 was charged into a reaction vessel equipped with a stirrer. The pH was adjusted to 6.5, and the temperature was raised to 55 ° C. While vigorously stirring the contents of the reaction vessel, Solution 2 and Solution 4 were each added at a rate of 90 ml/min for 0.67 minute. Solution 3 was then added to the mixture. Mercurous chloride antifoggant in the amount of 0.10 mg/Ag mole was then added to the portion Solution 4 that had not been added to the reaction vessel. The temperature of the reaction vessel was raised to 62 ° C, the pH was adjusted to 6.5, and the pCl was adjusted to 2.4. The mixture was held for five minutes. Following this hold, Solution 2 and Solution 4 were added simultaneously each at linearly accelerated rates of from 10 mL/min to 24 mL/min in 56 minutes with the pCl maintained at 2.4 and the pH maintained at 6.5. The mixture was then cooled to 40 ° C, and Solution 5 was added followed by stirring for five minutes. The pH was then adjusted to 3.8, and the gel allowed to settle. The liquid layer was decanted, and the depleted volume was restored with DW. The mixture was held until the temperature returned to 40 ° C. The pH was then adjusted to 4.2, and the mixture was held for 5 minutes before the pH was adjusted to 3.8. The settling and decanting steps were repeated. Solution 6 was added, and the pH and pCl were adjusted to 5.7 and 1.6, respectively.

Examination of the grain structure revealed that >80 percent of total grain projected area was accounted for by {100} tabular grains. The tabular grains lacked any identifiable non-{100} faces. The {100} tabular grains had a mean thickness of 0.14 µm and a mean equivalent circular diameter (ECD) of 1.48 µm.

Emulsion K

(example)

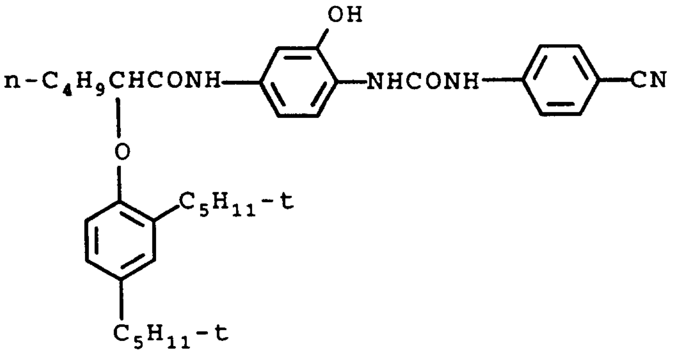
Emulsion K was prepared like Emulsion J, except that the precipitation was interrupted after 60% of the silver was introduced to allow the addition of a solution of 3.24 g NaSCN in 25 mL DW over 2 minutes.

Examination of the grain structure revealed that >80 percent of total grain projected area was accounted for by tabular grains with {100} major faces containing at least one identifiable non-{100} edge face. The tabular grains had a mean thickness of 0.16 µm and a mean equivalent circular diameter (ECD) of 1.28 µm.

Finishing, Coating and Sensitometry

Emulsions J and K were finished by adding 1 mole % NaBr, based on silver, followed by a 5 minute hold, a combination of the spectral sensitizing dyes anhydro-5-chloro-9-ethyl-5'-phenyl-3'-(3-sulfobutyl)-3-(3-sulfopropyl)oxacarbocyanine hydroxide, sodium salt (SS-3) and anhydro-11-ethyl-1,1'-bis(3-sulfopropyl)-naphtho[1,2-d]oxazolocarbocyanine hydroxide sodium salt (SS-4) (SS-3:SS-4 mole ratio 3:1) at 0.7 mmole/Ag mole followed by a 20 minute hold. Chemical sensitizers $Na_2S_2O_3 \cdot 5H_2O$ (2 mg/Ag mole) and $KAuCl_4$ (1 mg/Ag mole) were added followed by heating for 10 minutes at 60 °C. AMPT (100 mg/Ag mole) was added after the heating step.

The finished emulsions were coated at 8.55 mg Ag/dm^2 with a cyan dye-forming coupler CC-1 at 10.76 mg/dm^2. The coatings were overcoated with gel and hardened.



CC-1

Samples of the coatings were given an exposure of 1/50 sec through a graduated test object with simulated daylight and photographically processed for 60″, 90″ or 120″ in the Kodak Flexicolor ™ C-41 color negative process.

The sensitometric results are summarized in Table III. Speed measurements are the same as that reported in Table I. The Speed column in Table III reports the speed measured at 90 seconds of processing. Process sensitivity is the speed difference between the 60 and 120 second processing times.

Table III

Emulsion	SCN Dump	Speed	γ	Process Sensitivity
J	undoped	200	1.78	44
K	1.0 mole %	224	1.33	26

Emulsion K satisfying the requirements of the invention exhibited a higher speed and lower contrast than the control emulsion J. A significant further advantage for Emulsion K was its lower process sensitivity.

Example 5

This example demonstrates the effectiveness of thiocyanate and iodide employed in the same precipitation to produce non-{100} grain faces on high chloride tabular grains having {100} major faces.

Emulsion L

(example)

Eight solutions were prepared as follows:

Solution 1	
Gelatin (oxidized)	195 g
NaCl	3.0 g
D.W.	4369 g

Solution 2	
NaCl	420.4 g
DW to total volume	1799 mL

Solution 3	
NaCl	2.25 g
KI	0.60 g
DW	8983 g

Solution 4	
$AgNO_3$	1211.8 g
DW to total volume	1726 mL

Solution 5	
NaSCN	0.82 g
DW	25 g

Solution 6	
KI	5.93 g
DW	298 g

Solution 7	
Gelatin (phthalated)	215 g
DW	1500 g

Solution 8	
Gelatin (oxidized)*	81 g
DW	1500 g

*Treated with hydrogen peroxide to effectively eliminate methionine

Solution 1 was charged into a reaction vessel equipped with a stirrer. The pH was adjusted to 5.7 at a temperature of 35 ° C. While stirring the contents of the reaction vessel Solution 2 and Solution 4 were added each at 22.5 mL/min for 1.28 minutes. Solution 3 was then added to the mixture, and the pH was adjusted to 5.7. The mixture was held for eight minutes. Mercurous chloride antifoggant in the amount of 0.08 mg/Ag mole was then added to the portion Solution 4 that had not been added to the reaction vessel. Following this hold, Solution 2 was added at a constant rate of 9.8 ml/min while Solution 4 was added at linearly accelerated rates of from 12 mL/min to 12.1 mL/min in 2 minutes to raise the pCl to 2.6. The temperature was also linearly increased from 35 ° C to 36.5 ° C. Solution 2 and Solution 4 were then added simultaneously each at linearly accelerated rates of from 12.1 mL/min to 15 mL/min in 38 minutes with pCl maintained at 2.6. The temperature was also linearly increased from 36.5 ° C to 65 ° C. The mixture was held for twenty minutes. Following this hold, Solution 2 was added at linearly decelerated rates of from 16.5 mL/min to 16.2 mL/min, and Solution 4 was added at linearly accelerated rates of from 15 mL/min to 17.7 mL/min to drop pCl to 2.6. Solution 2 and Solution 4 were then added simultaneously at linearly accelerated rates of from 17.7 mL/min to 27.6 mL/min in 18.5 minutes with the pCl maintained at 2.6. Solution 5 was dumped into the reaction vessel and held for five minutes. Solution 2 and Solution 4 were then added simultaneously at linearly accelerated rates of from 27.6 mL/min to 36.5 mL/min in 16.8 minutes with the pCl maintained at 2.6. Solution 6 was then added to the mixture and held for ten minutes. Following this hold, Solution 2 and Solution 4 were added simultaneously at linearly accelerated rates of from 36.5 mL/min to 39 mL/min in 4.7 minutes with the pCl maintained at 2.6. The mixture was held for thirty minutes. Following this hold, the mixture was cooled to 40 ° C, and Solution 7 was added and stirred for five minutes. The pH was then adjusted to 3.8, and the gel was allowed to settle. The liquid layer was decanted, and the depleted volume was restored with DW. The mixture was held until the temperature returned to 40 ° C. The pH was then adjusted to 4.2, and the mixture held for five minutes before the pH was adjusted to 3.8. The settling and decanting steps repeated. Solution 8 was added, and the pH and pCl were adjusted to 5.7 and 1.6, respectively.

Examination of the grain structure revealed that >65 percent of total grain projected area was accounted for by tabular grains with {100} major faces containing at least one identifiable non-{100} edge face. The tabular grains had a mean thickness of 0.19 µm and a mean equivalent circular diameter (ECD) of 1.66 µm.

Finishing, Coating and Sensitometry

Emulsion L was finished, coated and sensitometrically examined similarly to Emulsion J. The performances of Emulsions J and L when processed for 120 seconds are compared in Table IV.

Table IV

Emulsion	**SCN & I Dump**	**Speed**	γ
J	undoped	200	1.95
L	1/4 & 1/2 M %	196	1.22

Emulsion L satisfying the requirements of the invention exhibited a significantly lower contrast than the control emulsion. The speed of Emulsion L was also somewhat lower than that of the control emulsion.

Examples 6 to 9

These examples demonstrate the capability of iodide to produce non-{100} grain faces on high chloride tabular grains with {100} major faces.

Example 6

This example demonstrates dumping iodide at the later stages of high chloride {100} tabular grain precipitation to produce non-{100} corner faces on the tabular grains.

Emulsion M

A 12 L reactor charged with 3.1 L of distilled water containing 2 g of NaCl and 130 g of oxidized gelatin was adjusted to pH 5.7 at 35°C. The contents of the reactor were stirred vigorously throughout the precipitation process. To the initially introduced solution were added simultaneously 1 M $AgNO_3$and 1 M NaCl solutions, each at a rate of 42 mL/min, each for 1.6 min. The pCl was maintained at 2.39 during nucleation.

A solution containing 5.8 L of distilled water, 190 g of 0.012 M KI solution, and 1.5g of NaCl was then added. The solution was allowed to sit for 5 minutes. After the hold, the mixture temperature was ramped from 35°C to 50°C in 20 minutes, and during the same time 4 M $AgNO_3$ and 4 M NaCl solutions were added at 10 mL/min each, with pCl ramped down from 2.39 to 2.24. The temperature was further ramped from 50°C to 65°C in 20 minutes, during which period the $AgNO_3$ and NaCl solutions were added at linearly accelerated rates of from 10 to 15 mL/min, with pCl linearly decreased from 2.2 to 1.82. After the ramp, the medium was allowed to sit at 65°C for 15 minutes. After the hold, addition of the $AgNO_3$ and NaCl solutions was resumed at linearly accelerated rates from 10 to 28.7 mL/min in 45 minutes. The pCl of the emulsion was held at 1.82 during the final growth period. Then the reactor was allowed to sit at 65°C for another 30 minutes.

After the hold, a 200 mL solution containing 4.96 g of KI was added, and the emulsion was allowed to sit for 10 minutes. Final grain growth was completed by adding 4 M $AgNO_3$ and NaCl solutions at 10 mL/min for 13 minutes with pCl controlled at 1.82.

The resulting emulsion had a mean grain size of 1.0 μm and mean grain thickness of 0.14 μm. Tabular grains having {100} major faces and visibly detectable non-{100} grain faces at their corners accounted for >84 percent of total grain projected area.

Example 7

This example demonstrates dumping and running iodide at the later stages of high chloride {100} tabular grain precipitation to produce non-{100} corner faces on the tabular grains.

Emulsion N

A 12 L reactor charged with 3.1 L of distilled water containing 2 g of NaCl and 130 g of oxidized gelatin was adjusted to pH 5.7 at 35°C. The contents of the reactor were stirred vigorously throughout the precipitation process. To the initially introduced solution were added simultaneously 1 M $AgNO_3$ and 1 M NaCl solutions, each at a rate of 45 mL/min, each for 1.6 min. The pCl was maintained at 2.39 during nucleation.

A solution containing 5.8 L of distilled water, 190 g of 0.012M KI solution, and 1.5g of NaCl was then added. The solution was allowed to sit for 5 minutes. After the hold, the mixture temperature was ramped from 35°C to 50°C in 20 minutes, and during the same time 4 M $AgNO_3$ and 4 M NaCl solutions were added at 10 mL/min each, with pCl ramped down from 2.39 to 2.24. The temperature was further ramped from 50°C to 65°C in 20 minutes, during which period the $AgNO_3$ and NaCl solutions were added at linearly accelerated rates of from 10 to 15 mL/min, with pCl linearly decreased from 2.2 to 1.82. After the ramp, the medium was allowed to sit at 65°C for 15 minutes. After the hold, additions of the $AgNO_3$ and NaCl solutions were resumed at linearly accelerated rates of from 10 to 22 mL/min in 30 minutes. The pCl of the emulsion was held at 1.82 during the final growth period. Then the reactor was allowed to sit at 65°C for another 30 minutes. After the hold, a 200 mL solution containing 4.96 g of KI was added, and the emulsion was allowed to sit for 10 minutes. Final growth was completed by adding 4 M $AgNO_3$, and 4 M NaCl and 0.12 M KI solutions were each introduced at 10 mL/min for 10 minutes with pCl controlled at 1.82.

The resulting emulsion had a mean grain size of 1.1 μm and thickness of 0.13 μm. Tabular grains having {100} major faces and visibly detectable non-{100} grain faces at their corners accounted for >70 percent of total grain projected area.

Example 8

This example demonstrates dumping iodide at the later stages of high chloride {100} tabular grain precipitation to produce non-{100} corner faces on the tabular grains.

Emulsion O

A 12 L reactor charged with 3.1 L of distilled water containing 2 g of NaCl and 130 g of oxidized gelatin was adjusted to pH 5.7 at 35 ° C. The contents of the reactor were stirred vigorously throughout the precipitation process. To the initially introduced solution were added simultaneously 1 M $AgNO_3$ and 1 M NaCl solutions, each at a rate of 52 mL/min, each for 1.6 min. The pCl was maintained at 2.39 during nucleation.

A solution containing 5.8 L of distilled water, 190 g of 0.012 M solution, and 1.5 g of NaCl was then added. The solution was allowed to sit for 5 minutes. After the hold, the mixture temperature was ramped from 35 ° C to 65 ° C in 30 minutes and during the same time 1 M $AgNO_3$ and 1 M NaCl solutions were added at 10 mL/min each, with pCl ramped down from 2.39 to 1.82. After the ramp, the medium was allowed to sit at 65 ° C for 60 minutes.

After the hold, a 200 mL solution containing 4.96 g of KI was added, and the emulsion was allowed to sit for 10 minutes. Final growth was completed by adding 1 M $AgNO_3$ and 1 M NaCl solutions at 10 mL/min for 10 minutes with pCl controlled at 1.82.

The resulting emulsion had a mean grain size of 1.04 μm and thickness of 0.07 μm. Tabular grains having {100} major faces and visibly detectable non-{100} grain faces at their corners accounted for >90 percent of total grain projected area.

Example 9

This example demonstrates running iodide at the later stages of high chloride {100} tabular grain precipitation to produce high chloride {100} tabular grains with at least one non-{100} grain face.

Emulsion P

An 18 L reactor charged with 4.368 L of distilled water containing 3.0 g of NaCl and 195.0 g of oxidized gelatin was adjusted to pH 5.7 at 35 ° C. The contents of the reactor were stirred vigorously throughout the precipitation process. To the initially introduced solution were added simultaneously 1 M $AgNO_3$ at 78 mL/min and 4 M NaCl at 20 mL/min for 1.6 min, while the pCl was maintained at 1.97.

Then 9.285 L of a solution containing 2.25 g NaCl and 0.65 g of KI was added to the reaction vessel. The solution was allowed to sit for 5 minutes. After the hold, the solution temperature was ramped from 35 to 36.5 ° C in 2 minutes, and the pCl was ramped from 2.19 to 2.35, while 4 M $AgNO_3$ containing 0.08 mg mercuric chloride per mole of silver nitrate and 4 M NaCl were delivered to the reaction vessel at 15 mL/min. During the next 18 minutes, 4 M $AgNO_3$ containing 0.08 mg mercuric chloride per mole of silver nitrate and 4 M NaCl were added at 15 mL/min while the pCl was linearly ramped from 2.35 to 2.21 and the temperature was ramped from 36.5 to 50 ° C. During the following 20 minutes, 4 M $AgNO_3$ containing 0.08 mg mercuric chloride per mole of silver nitrate and 4 M NaCl were added at linearly accelerated rates of from 15 to 22.5 mL/min, with pCl linearly decreasing from 2.21 to 1.72, and the temperature was linearly raised from 50 to 70 ° C. After the ramp, the medium was allowed to sit at 70 ° C for 15 minutes.

After the hold, 4 M $AgNO_3$ containing 0.08 mg mercuric chloride per mole of silver nitrate and 4 M NaCl were added at linearly accelerated rates of from 15 to 38.6 mL/min over 37.4 minutes, while the pCl was maintained at 1.72. After this ramp, the medium was allowed to sit at 70 ° C for 30 minutes. Final growth was completed by adding 4 M $AgNO_3$ containing 0.08 mg mercuric chloride per mole of silver nitrate, and a salt solution which was 3.72 M NaCl and 0.28 M KI was added to the reaction vessel at 20 mL/min each while the pCl was maintained at 1.72.

The resulting emulsion had a mean grain size of approximately 1.6 μm and mean grain thickness of approximately 0.16 μm. Tabular grains having {100} major faces and visibly detectable non-{100} grain faces at their corners accounted for >50 percent of total grain projected area.

Example 10

This example demonstrates the preparation of high chloride {100} tabular grain emulsions with edge modifications to provide non-{100} grain faces being provided by an adsorbed organic grain growth modifier.

Host Emulsion H-A

A high chloride {100} tabular grain emulsion was made using the procedures given in House et al U.S. Patent 5,320,938. The tabular grains had a mean equivalent circular diameter of 2.5 µm and a mean thickness of 0.16 µm. No visibly identifiable non-{100} grain faces were present.

Host Emulsion H-B

A high chloride {100} tabular grain emulsion was prepared similar as Host Emulsion H-A. The tabular grains had a mean equivalent circular diameter of 1.5 µm and a mean thickness of 0.13 µm. No visibly identifiable non-{100} grain faces were present.

Emulsion Q High-Chloride {100} Tabular Grains with {111} Corner Faces, 13 Mole % Overgrowth Using 4,5,6-Triaminopyrimidine as Grain Growth Modifier

To a stirred reaction-vessel containing 0.04 mole of Host Emulsion H-B in 400 mL of a solution at pH 6.0 and at 40 °C that was 2% in bone gelatin, 2.0 mM in 4,5,6-triaminopyrimidine, and 0.040 M in NaCl were added 3.0 mL of 2 M $AgNO_3$ solution at 1.0 mL/min and 2.5 M NaCl solution at a rate needed to maintain a constant pCl of 1.50.

The resulting emulsion was examined by scanning electron microscopy. Greater than 60 percent of total grain projected area was provided by high chloride {100} tabular grains having two sloping faces adjacent each corner. No protrusions above the {100} major faces of the tabular grains were observed. Examination of grain corners at appropriate angles revealed the angle between the two sloping corner faces to be approximately 109° confirming that they are {111} faces. (With this identification, the orientation of the grain's crystal lattice relative to its shape was established and, from this, the orientation of the edge faces perpendicular to the {100} major faces, comparable to faces **306-312** in grain **300** were confirmed to be {100} rather than {110} faces. Thus, the grain was essentially similar to ideal grain structure **300**.)

Emulsion R High-Chloride {100} Tabular Grains with {111} Corner Faces, 23 Mole % Overgrowth Using 2,4,6-Triiodophenol as Grain Growth Modifier

To a stirred reaction vessel containing 0.04 mole of Host Emulsion H-B in 400 mL of a solution at pH 6.0 and at 60 °C that was 2% in bone gelatin, 0.2 mM in 2,4,6-triiodophenol, 0.040 M in NaCl, and 0.20 M in sodium acetate were added 3.0 mL of 4 M $AgNO_3$ solution at 1.0 mL/min and 4.5 M NaCl solution at a rate needed to maintain a constant pCl of 1.42.

The resulting emulsion was examined by scanning electron microscopy. It consisted of high chloride {100} tabular grains having two sloping faces adjacent at each of their corners and no protrusions above the {100} major faces of the tabular grains. Examination of grain corners at appropriate angles revealed the angle between the two corner faces to be approximately 109° confirming that they are {111} faces.

Emulsion S High-Chloride {100} Tabular Grains with {110} Corner and Edge Faces, 23 Mole % Overgrowth Using 1-(3-Acetamidophenyl)-5-mercaptotetrazole as Grain Growth Modifier

This emulsion was prepared similarly to that of Emulsion R, except the reaction vessel was made 0.30 mM in 1-(3-acetamidophenyl)-5-mercaptotetrazole and no triiodophenol was added.

The resulting {100} tabular grains had {110} faces along their edges and corners; twelve {110} faces per grain. Thus, the tabular grains were similar to ideal grains **200**.

Emulsion T (failure) High-Chloride Non-{100} Tabular Grains with {110} Corner and Edge Faces, 23 Mole % Overgrowth

This emulsion was prepared similarly to that of Emulsion R, 2 except that the reaction vessel was made 0.20 mM in 5-carboxy-4-hydroxy-6-methyl-2-methylthio-1,3,3a,7-tetraazaindene and no triiodophenol was added.

Rectangular tabular grains were observed. The edges and corners of the rectangular tabular grains consisted of twelve {110} faces per grain. However, no {100} major faces were in evidence. The major faces of the grains were clearly ruffled, indicative of a grain surface formed by non-{100} pyramidal deposits of the type described by Maskasky U.S. Patent 4,643,966. This demonstrated the ineffectiveness of the tetraazaindene grain growth modifier to produce emulsions satisfying the requirements of the invention.

Emulsion U (failure) High-Chloride Non-{100} Tabular Grains with {110} Corner and Edge Faces, 23 Mole % Overgrowth

This example was prepared similarly to that of Emulsion R, except that the reaction vessel was made 0.30 mM in 2-mercaptopyridine and no triiodophenol was added.

The resulting rectangular tabular grains did not contain major {100} faces. The grains exhibited surface features similar to those described above fore Emulsion T.

Emulsion V (failure) High-Chloride Non-{100} Tabular Grains with {110} Corner and Edge Faces, 23 Mole % Overgrowth

To a stirred reaction vessel containing 0.04 mole of Host Emulsion H-A in 400 mL of a solution at pH 6.2 and at 75°C that was 2% in bone gelatin, 3.9 mM in adenine, 0.037 M in NaCl, and 0.20 M in sodium acetate were added 15.0 mL of 4 M $AgNO_3$ solution at 1.0 mL/min and 4.5 M NaCl solution at a rate needed to maintain a constant pCl of 1.43.

The resulting emulsion was examined by scanning electron microscopy. The resulting grains had ruffled surfaces and {111} corner faces. No {100} major faces were observed.

Claims

1. A radiation sensitive emulsion containing a silver halide grain population comprised of at least 90 mole percent chloride, based on silver, wherein at least 50 percent of the total grain population projected area is accounted for by tabular grains
   (1) bounded by parallel major faces lying in {100} atomic planes and having adjacent edge ratios of less than 10 and
   (2) having a thickness of less than 0.2 µm, characterized in that each of the tabular grains accounting for at least 50 percent of the total grain projected area
   (3) contains at least one crystal face that lies in an atomic plane differing from that of the major faces and
   (4) exhibits a lower grain volume than a tabular grain of the same length, width and thickness bounded entirely by crystal faces lying in {100} atomic planes.

2. A radiation sensitive emulsion according to claim 1 further characterized in that the crystal face that lies in an atomic plane differing from that of the major faces is a sloping face located adjacent a grain corner.

3. A radiation sensitive emulsion according to claim 2 further characterized in that the tabular grains accounting for at least 50 percent of total grain projected area contain a sloping face located adjacent each grain corner or edge.

4. A radiation sensitive emulsion according to claim 2 or 3 further characterized in that the sloping face lies in a {111} or {110} atomic plane.

5. A radiation emulsion according to any one of claims 2 to 4 inclusive further characterized in that the tabular grains with at least one sloping face contain iodide.

6. A radiation sensitive emulsion according to any one of claims 2 to 5 inclusive further characterized in that the emulsion contains a thiocyanate.

7. A radiation sensitive emulsion according to any one of claims 1 to 6 inclusive further characterized in that one of the crystal faces that lies in an atomic plane differing from that of the major faces is larger than any other crystal face lying in a like atomic plane.

8. A radiation sensitive emulsion according to any one of claims 1 to 6 inclusive further characterized in that the tabular grains accounting for at least 50 percent of total grain projected area are comprised of tabular grains each containing eight equivalent crystal faces lying in like atomic planes that differ from {100} atomic planes.

9. A radiation sensitive emulsion according to claim 8 further characterized in that a grain growth modifier is preferentially adsorbed to each crystal face that lies in an atomic plane differing from that of the major faces.

FIG. 1A

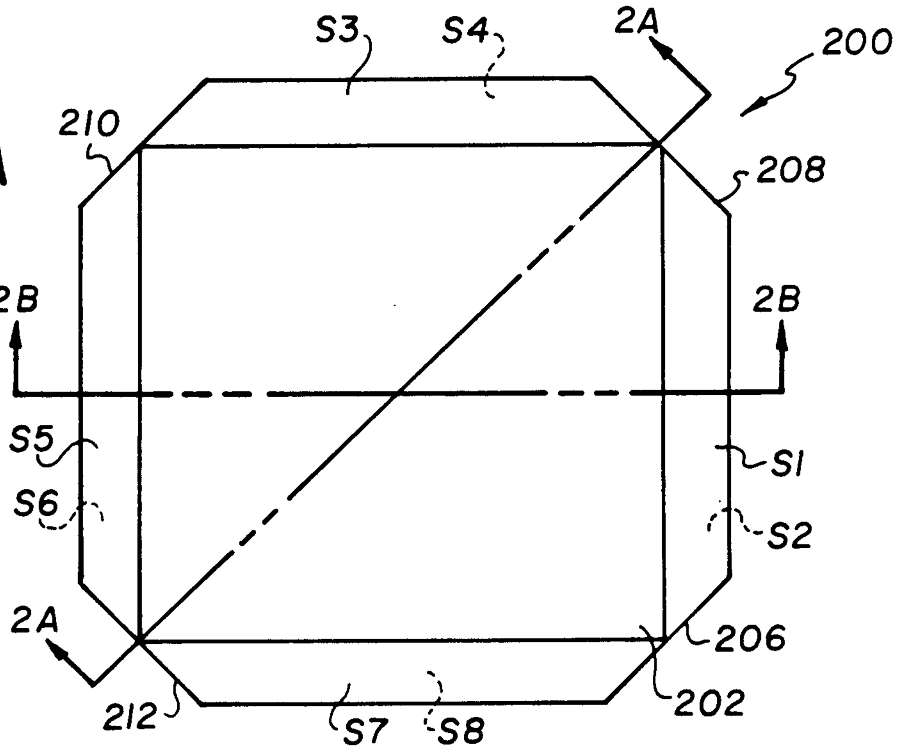

S3
S4
2A
200
210
208
2B
2B
S5
S1
S6
S2
2A
206
212
202
S7
S8

FIG. 1B

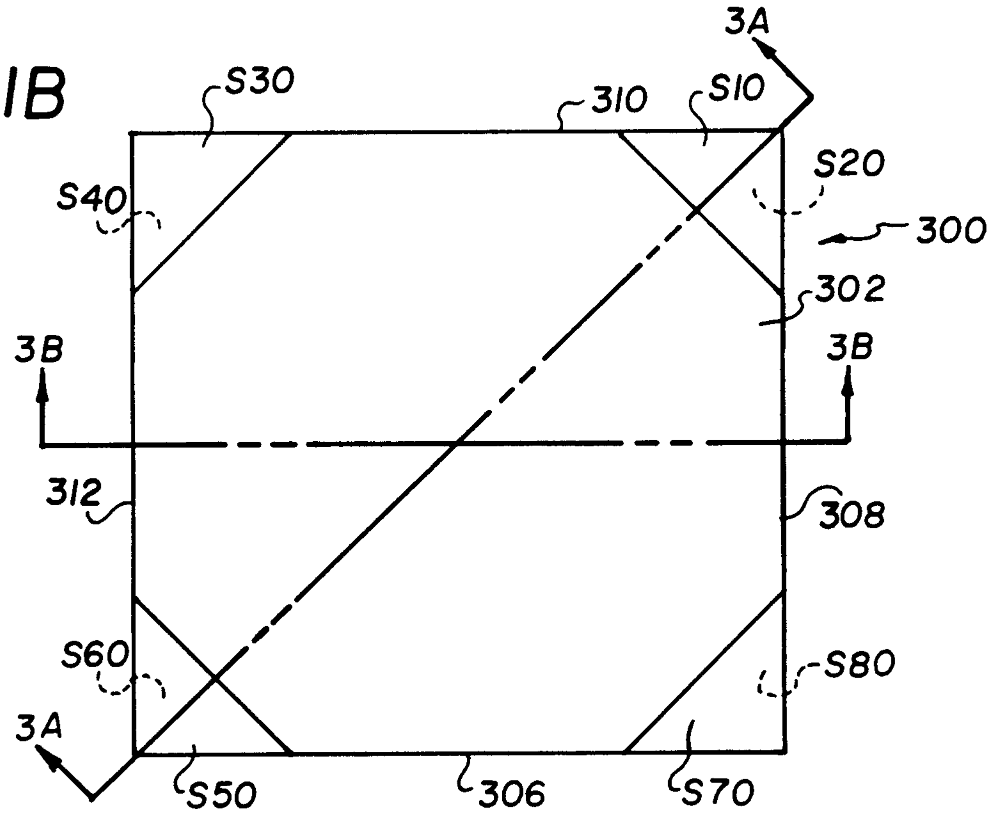

3A
S30
310
S10
S20
S40
300
302
3B
3B
312
308
S60
S80
3A
S50
306
S70

FIG. 2A

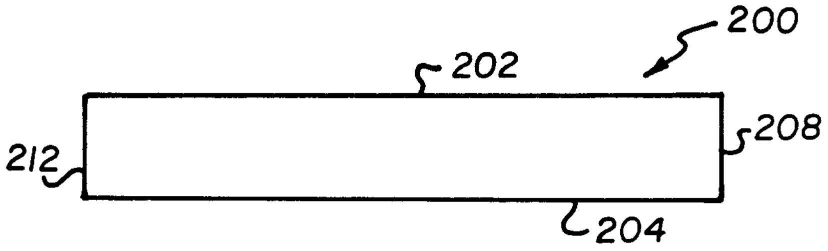


FIG. 2B

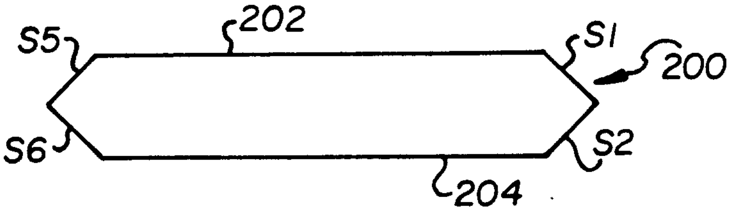


FIG. 3A

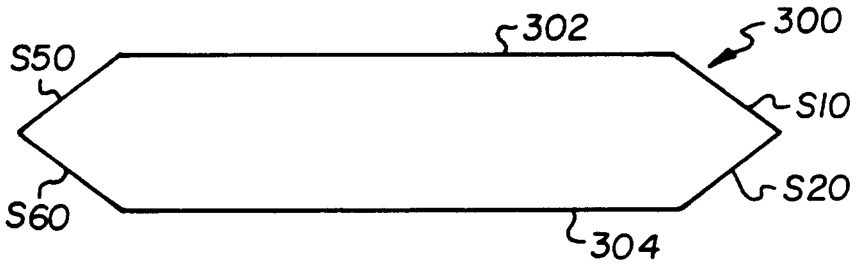


FIG. 3B

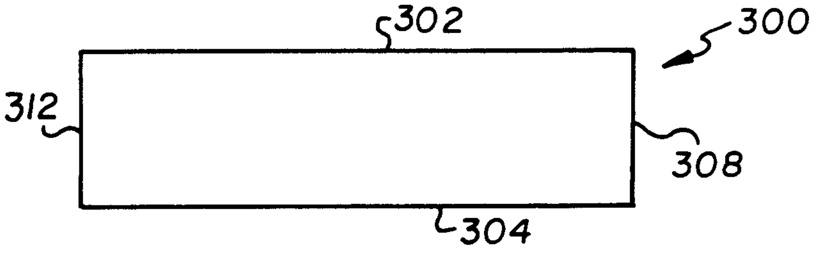


FIG. 4
(PRIOR ART)

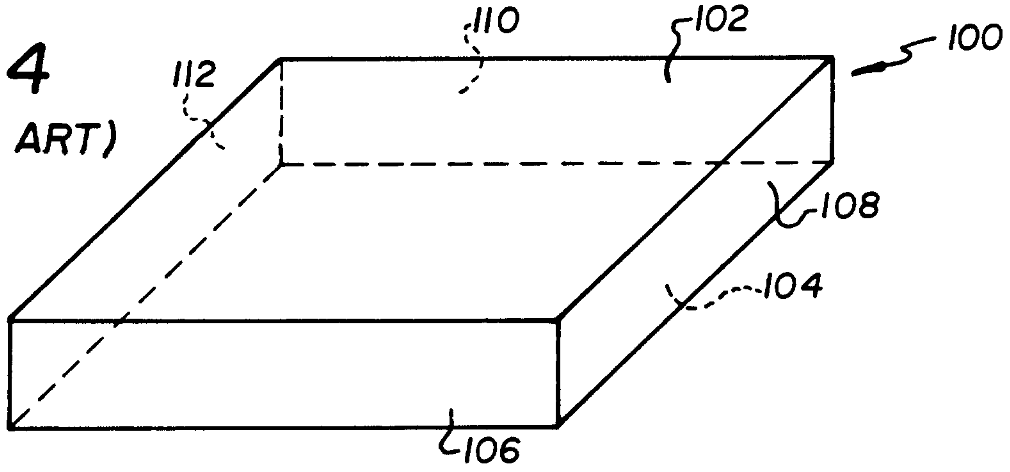


FIG. 5