

United States Patent

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[54] PREPARATION OF SILVER HALIDE GRAINS

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Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 500,366, Oct. 21, 1965, abandoned.
- [52] U.S. Cl. **96/108, 96/94**
- [51] Int. Cl. **G03c 1/28, G03c 1/02**
- [58] Field of Search **96/108, 94, 107, 106**

[56] References Cited

OTHER PUBLICATIONS

E. Klein in The Journal of Photographic Science, Ia: Properties of Photographic Emulsions Grains, Vol. 12, 1964, pages 242-251

"Effects of Environment on the Growth of Silver Bromide Microcrystals," by Berry et al., Photographic Science and Engineering, Vol. 5, No. 6, Nov.-Dec. 1961, pages 332-336.

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[57] ABSTRACT

Photographic emulsions comprising cubic-regular grains free of reduction sensitization are prepared by running an aqueous solution of silver nitrate and an aqueous solution of a silver halide simultaneously into an agitated aqueous solution of a peptizer in a double-run precipitation procedure while maintaining the pH at no more than 4.0 and the pAg at a value within the range of 8.6 to 9.1. In one aspect of this invention, emulsions prepared by the above procedure are chemically sensitized with a compound containing a labile atom selected from the group consisting of sulfur, selenium and tellurium and spectrally sensitized with a cyanine dye having an anodic half-wave potential less than 1.0 volt and a cathodic half-wave potential less than -0.8 volt.

14 Claims, No Drawings

PREPARATION OF SILVER HALIDE GRAINS

This application is a continuation-in-part of U.S. Pat. Ser. No. 500,366 filed Oct. 21, 1965 and now abandoned.

This invention relates to a method of preparing silver halide grains of cubic-regular shape substantially free of reduction sensitization and sensitized photographic emulsions prepared from those grains.

In the conventional making of silver halide grains, grains are obtained of irregular shapes, the crystal faces of which are in general (1,1,1). These grains experience a certain amount of reduction sensitization in their preparation. When emulsions prepared from silver halide grains of conventional type are spectrally sensitized, the sensitizing dye is prone to desensitize the grains in the blue region of the spectrum. Moreover, sulfur- and gold-sensitizing of emulsions which were reduction-sensitized during grain preparation results in high fog.

One object of my invention is to provide a method of preparing silver halide grains of cubic-regular shape and free of the effects of reduction sensitization. Another object of my invention is to provide photographic emulsions prepared from silver halide grains of cubic-regular type which are readily susceptible to sensitizing by sensitizing agents without adverse effects upon certain regions of sensitivity. A further object of my invention is to provide cubic-regular grained silver halide emulsions sensitized with sulfur-type chemical sensitizers and optionally with noble metal-type and/or spectral sensitizer. Other objects of my invention will appear herein.

Silver bromide or chloride is ordinarily prepared in the form of fine crystals or grains which have cubic structures. The faces of these crystals are generally (1,1,1), even though the lattice structure is cubic. Grains presenting cubic faces are not common and do not result from the usual conventional methods of making silver halide. Such grains in which the (1,0,0) faces are predominant will be referred to herein as "cubic-regular." By carrying out the preparation of the silver halide grains under certain special conditions, "cubic-regular" grains are obtained.

The emulsions of this invention can contain some silver halide grains which are not regular; however, when such grains are present, they generally do not constitute more than about 20 percent, by weight, of the grains smaller than the mean grain size and/or more than about 20 percent, by number, of the grains larger than the mean grain size. Preferred emulsions prepared according to this invention comprise silver halide grains of which at least about 80 percent, often at least about 90 or 95 percent, by weight, are regular. Silver halide emulsions in which a major portion of the grains have a regular structure or shape are known. As disclosed in a paper entitled "Fundamental Aspects of Growth and Shape of Photographic Silver Halide Crystals," published in *The Proceedings of the 5th International Conference on Nuclear Photography* held at Cern, Geneva, Sept. 15-18, 1965, edited by E. Dahl-Jensen, regular silver halide grains or crystals are obtained by isotropic growth occurring simultaneously and uniformly on all crystal faces. Such crystals develop (1,0,0) or (1,1,1) faces and are free of twin plane stacking faults, e.g., twin planes such as (1,1,1) twin planes. A (1,1,1) twin plane is a stacking fault which arises when a silver halide crystal grows in such a manner as to alter the previously established order of stacking of (1,1,1) planes in forming the crystal.

Photographic silver halide emulsions comprising silver halide grains of regular shape or structure can be obtained by controlling the reaction conditions during the phase of crystal growth. Depending upon these conditions, the regular silver halide grains will be characterized by a certain crystal habit, e.g., cubic, cubo-octahedral and/or octahedral, and will exhibit certain planes, e.g., (1,0,0) or (1,1,1) planes, as crystal faces. For example, in an article entitled "Precipitation of Twinned AgBr Crystals," by Berry and Skillman, *Photographic Science and Engineering*, Vol. 6, No. 3, May-June, 1962, it is shown that by a change in pAg it is possible to conduct a double-run precipitation of silver halide in such a manner that regular cubes or octahedra are formed. In a double-run procedure, the silver halide grains are prepared by simultane-

ously running an aqueous solution of a water-soluble silver salt, for example, silver nitrate, and a water-soluble halide, for example, an alkali metal halide such as potassium bromide, into a rapidly agitated aqueous solution of a silver halide peptizer, preferably gelatin, a gelatin derivative or some other protein peptizer. To obtain substantially regular grains, a large excess of halide ion is generally avoided. The conditions employed during the preparation of the silver halide grains are interrelated and a change in one variable such as pAg, pH, etc., while maintaining other conditions constant can change the silver halide crystal structure. In addition to previous references, a suitable method for preparing photographic silver halide emulsions having the required regular shape is also disclosed in an article entitled "Ia: Properties of Photographic Emulsion Grains," by Klein and Moisar, *The Journal of Photographic Science*, Vol. 12, 1964, pages 242-251. A prepared class of photographic silver halide emulsions employed in the practice of this invention contains silver halide grains in which (1,0,0) faces predominate. Such silver halide grains are referred to herein as "cubic-regular" grains.

According to this invention, I have now found that if cubic-regular grains are formed in a peptizer solution having a pH of 4 or less, reduction sensitization of the grains is avoided. In one embodiment, I have found that these grains when sensitized with sulfur-type and noble metal-type sensitizers show a greater increase in speed upon spectral sensitization than silver halide grains which are not of this type. Sulfur-type sensitizers include all compounds utilizing sensitization of photographic emulsions with an element from the sulfur group, e.g., sulfur, selenium or tellurium.

The method of preparing silver halide grains in accordance with my invention is carried out by running aqueous solutions of silver nitrate and of water-soluble halide simultaneously into a rapidly agitated aqueous solution of a peptizer such as gelatin or gelatin derivative, preferably at a temperature between 30° and 90° C., the pH being maintained at 4.0 or less with sulfuric or equivalent acid, the reactants being so added that the pAg is maintained at a value within the range of 8.6 to 9.2. Quantities of halide ion greatly in excess of silver ion in the mass should be avoided.

The silver halide grains thus prepared are useful in preparing photographic emulsions. When a gelatin derivative is employed as the peptizer, the grains obtained can be conveniently washed by the grain-wash method described in Yutzy and Frame, U.S. Pat. No. 2,614,928, which grains are useful in making a "washed" emulsion. Conversely, the silver halide dispersion prepared as described can be used directly for making an emulsion by mixing with protective colloid for the silver halide grains.

To the emulsion may be added various addenda including sulfur-type sensitizers, i.e., sulfur sensitizer, selenium sensitizer or tellurium sensitizer as described in Sheppard, U.S. pat. Nos. 1,574,944 and 1,623,499, and Petz, German Pat. No. 1,151,174; noble metal-type sensitizers such as gold sensitizers as described in U.S. pat. Nos. 2,399,083, 2,448,060 and 2,642,361; coating aids; hardeners; antifoggants; antiplumming agents; etc.

Also added to the emulsion is a spectral sensitizer. Particularly good results are obtained with organic cyanine dyes having a high resistance to reduction but which are easily oxidized; that is, the dyes should have a cathodic polarographic half-wave potential (E_c) less than -0.8 volt and an anodic half-wave potential (E_a) less than 1.0 volt. Preferably E_a is less than 0.9 and E_c is less than -1.1. Cathodic measurements can be made with a 1×10^{-4} molar solution of the spectral sensitizer in a solvent, for example, methanol which is 0.05 molar in lithium chloride using a dropping mercury electrode with the polarographic half-wave potential for the most positive cathodic wave being designated E_c . Anodic measurements can be made with 1×10^{-4} molar aqueous solvent solution, for example, methanolic solutions of the spectral sensitizer which are 0.05 molar in sodium acetate and 0.005 molar in acetic acid using a carbon paste of pyrolytic graphite electrode, with

the voltammetric half-peak potential for the most negative anodic response being designated E_a . In each measurement, the reference electrode can be an aqueous silver — silver chloride (saturated potassium chloride) electrode at 20° C. Electrochemical measurements of this type are known in the art and are described in *New Instrumental Methods in Electrochemistry*, by Delahay, Interscience Publishers, New York, New York, 1954; *Polarography*, by Kolthoff and Lingane, 2nd Edition, Interscience Publishers, New York, New York, 1952; *Analytical Chemistry*, 36, 2426 (1964) by Elving; and *Analytical Chemistry*, 30, 1576 (1958) by Adams. Plus and minus signs are according to IUPAC (International Union of Pure and Applied Chemistry) Stockholm Convention 1953. A cyanine dye sensitizer, especially one containing an acid radi-

tion is taken and given no spectral sensitization and two other portions are given spectral sensitization, one being sensitized to green with an oxacarbocyanine dye as described in U.S. Pat. No. 2,688,545 and the other to red with a thiocarbocyanine dye as described in U.S. Pat. No. 2,704,714. Each of the twelve emulsions are coated on cellulose acetate supports at the rate of 100 mg. silver and 315 mg. of gelatin per square foot. The coatings are exposed on an Eastman 1B sensitometer for one-fifth of a second to a Positive lamp plus a color chart and developed 6 minutes in Kodak Rapid X-ray Developer, after which they are subjected to a stop bath and a fixing bath and are washed and dried in that order. The speeds of each of the products are measured with the following results:

Cubic-regular bromolodide emulsion	Clear	Blue ¹	Green ²	Red ³
Sulfur- and gold-sensitized spectral sensitization:				
Green.....	182	25		
Red.....	1,590	46	209	
.....	3,160	46		2,000
Reduction-sensitized spectral sensitization:				
Green.....	100	15		
Red.....	398	11.5	46	
.....	417	8.9		240
Irregular-octahedral bromolodide emulsion				
Sulfur- and gold-sensitized spectral sensitization:				
Green.....	575	76		
Red.....	1,200	30	145	
.....	1,100	18		631
Reduction-sensitized spectral sensitization:				
Green.....	289	42		
Red.....	832	25	91	
.....	759	13.2		417

¹ Blue speeds are obtained using Kodak Wratten Filters #35 and #38A and are considered to be a valid measure of the basic blue sensitivity of a bromolodide emulsion.

² Wratten #31 and #16 Filters.

³ Wratten #23 Filter.

cal, is preferred. Examples of useful spectral sensitizers are those described in U.S. pat. Nos. 2,688,545 and 2,704,714. I have found that emulsions prepared as described when chemically sensitized such as with sulfur and gold sensitizers give much better speeds upon spectral sensitization than is the case with either emulsions having other than cubic-regular silver halide grains or with emulsions composed of cubic-regular silver halide grains which have been subjected to reduction sensitization. I have found that desensitization in the region of blue sensitivity often encountered in spectrally sensitizing silver halide emulsions is inhibited when spectral sensitizers are added to emulsions composed of cubic-regular silver halide grains which have not been reduction-sensitized.

The following examples further illustrate preferred embodiments of the invention, although it will be understood that the examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise indicated.

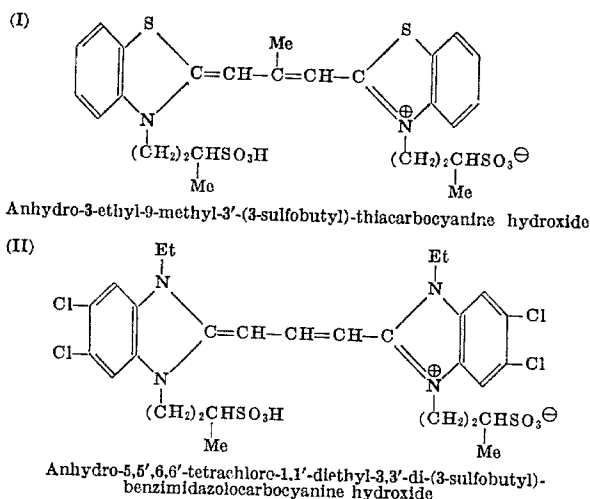
EXAMPLE 1:

An aqueous solution of potassium bromide and potassium iodide and an aqueous solution of silver nitrate in equal molar amounts are added simultaneously to a rapidly agitated aqueous gelatin solution maintained at a temperature of 70° C., the addition being carried out over a period of 35 minutes. The pH of the aqueous gelatin solution is maintained at 2.0 by occasional additions of sulfuric acid and the pAg is maintained at 9.0 by adjusting the relative rates of addition of the halide and silver nitrate solutions. There is obtained a dispersion of cubic-regular grain silver bromoiodide crystals having an average grain size of about 0.2 micron. The emulsion is washed and a protective colloid is added in the form of an aqueous gelatin solution. One portion of the emulsion is sulfur- and gold-sensitized as described in Waller, U.S. Pat. No. 2,399,083, and another portion is reduction-sensitized as described in Allen et al, U.S. Pat. No. 2,983,609. An irregular octahedral-grained silver bromoiodide emulsion is also divided into two portions, one of which is sulfur- and gold-sensitized and the other reduction-sensitized. In each case a por-

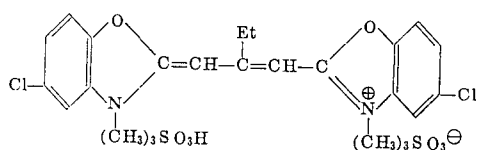
The sulfur- and gold-sensitized cubic-regular silver bromoiodide emulsion shows a large increase in speed on spectral sensitization accompanied by an increase in blue speed, while the reduction-sensitized cubic-regular bromoiodide and the irregular-octahedral-grained bromoiodide emulsions, either sulfur- and gold-sensitized or reduction-sensitized, show a smaller increase in speed, partly due to blue-speed loss on spectral sensitization.

EXAMPLE 2

A sulfur-gold-sensitized cubic-regular-grained silver bromoiodide emulsion is prepared as described in Example 1. The emulsion is divided into several portions which are spectrally sensitized with the following sensitizing dyes:

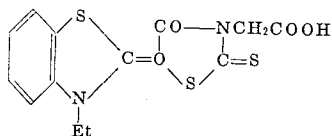


(III)



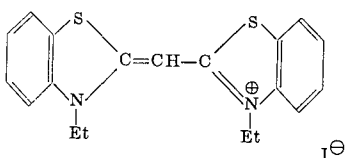
Anhydro-5,5-dichloro-9-ethyl-3,3'-di(3-sulfopropyl)-oxacarbocyanine hydroxide, sodium salt

(IV)



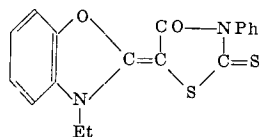
3-carboxymethyl-5-(3-ethyl-2(3)-benzothiazolylidene)-rhodanine

(V)



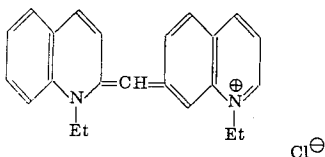
2,2'-diethylthiacyanine iodide

(VI)



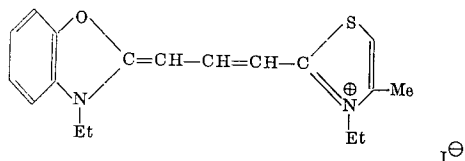
5-(2-ethyl-1(2)-benzoxazolylidene)-3-phenylrhodanine

(VIII)



1:1'-diethyl-2,2'-cyanine chloride

(VIII)



2,3'-diethyl-4'-methyloxathiazolocarbocyanine iodide
Each portion is coated on a film support as described in Example 1. A sample of each coating is exposed on a sensitometer at 365 mμ, processed for 4 minutes in Kodak Developer D-19, fixed, washed and dried with the following results:

Sensitizing Dye	mg. dye/ mole AgX	E _a ⁽¹⁾ of dye	E _c ⁽²⁾ of dye	Relative Speed
None	—	—	—	100
Dye I	500	+0.73	-1.29	302
Dye II	760	+0.52	-1.60	257
Dye III	640	+0.95	-1.26	178
Dye IV	690	+0.86	-1.60	437
Dye V	960	+1.05	-1.38	152
Dye VI	730	+0.89	-1.72	145
Dye VII	500	+0.95	-1.08	100
Dye VIII	500	+0.70	-1.33	191

(1) E_a is determined on a polarograph using a methanol solution of the dye and a carbon paste electrode vs. a Ag/AgCl electrode in saturated KCl.

(2) E_c is determined on a polarograph using a methanol solution of the dye and a dropping mercury electrode vs. a Ag/AgCl electrode in saturated KCl.

It can be seen from the above comparison that highest blue speeds are obtained with cyanine dyes having an anodic half-

wave potential (E_a) less than 1.0 volt and a cathodic half-wave potential (E_c) less than -0.8 volt; with the best dyes E_a is less than 0.9 and E_c is less than -1.1 volts.

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EXAMPLE 3

The presence of reduction sensitizing can be observed by comparing blue speeds of comparative emulsions. It is well-known that reduction sensitizing increases emulsion speed as described in Allen and Lowe, U.S. Pat. No. 2,983,609.

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Two emulsions are made according to Example 1 with a pAg of 8.8 and a pH of 2 and 5.6 respectively. The emulsions are coated and given a long exposure of 10 seconds, developed for 5 minutes in Kodak DK-50 Developer, fixed, washed and dried. The results in the table below demonstrate an increased emulsion speed for the emulsion made at a pH of 5.6 which is apparently due to reduction sensitizing, whereas the emulsion prepared at a pH of 2.0 has a lower speed.

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Emulsion Preparation pH
2.0
5.6

Relative Blue Speed
100
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EXAMPLE 4

25 Cubic-regular emulsions prepared at a pH of 2.0 are spectrally sensitized more effectively than emulsions prepared at a pH of 5.6.

Comparative cubic-regular grain emulsions are made according to Example 1 wherein the pAg is controlled at 8.8 and the pH at 2.0 and 5.6 respectively. Samples of each of the respective emulsions serve as controls. Other portions of the respective emulsions are spectrally sensitized, one being sensitized to the green region of the spectrum with 400 mg. of a benzimidazolocarbo-cyanine dye as described in U.S. Pat. No. 2,945,763 and one other portion of each emulsion to the red region of the spectrum with 400 mg. of a thiocarbo-cyanine dye of the type described in U.S. Pat. No. 2,917,516. Each emulsion is coated, exposed for 10 seconds to blue and white light as in Example 1, processed in Kodak DK-50 Developer, fixed, washed and dried.

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Emulsion Preparation pH	Spectral Sensitization	Relative Speeds Blue Clear
2.0	—	100 100
2.0	green	78 363
2.0	red	62 407
5.6	—	100 100
5.6	green	23 94
5.6	red	32 80

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EXAMPLE 5

65 Spectrally sensitized cubic emulsions prepared at a pH of 5.6 and which have been sulfur- and gold-sensitized exhibit high fog compared to similar emulsions prepared at a pH of 2.0.

Portions of separate emulsions prepared according to Example 1 at pAg of 8.8 and a pH of 2.0 and 5.6 respectively and which have been sulfur- and gold-sensitized according to Example 1 are spectrally sensitized as in Example 4 with one sample serving as a control for each emulsion. The emulsions are coated, exposed for one-fifth second to blue and white light as in Example 1, processed in Kodak DK-50 Developer, fixed, washed and dried. The results are demonstrated in the following table:

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Emulsion Preparation	Spectral Sensitization	Relative Speeds		Fog
		Blue	Clear	
pH 2.0	—	100	100	.04
2.0	green	129	575	.04
2.0	red	204	1150	.04
5.6	—	89	82	.91
5.6	green	170	813	.97
5.6	red	135	725	.79

It is apparent that the spectrally sensitized sulfur- and gold-sensitized cubic-grained emulsions made at a pH of 5.6 provide heavy fog, whereas the same emulsion made at a pH of 2.0 is effectively spectrally sensitized without the formation of fog.

EXAMPLE 6

Cubic-grained emulsions which are made at a pH of 2.0 are sensitized more effectively to the infrared region of the spectrum than comparative emulsions prepared at a pH of 5.6.

Sulfur- and gold-sensitized emulsion samples are prepared as described in Example 5, except that infrared sensitizers are used in place of the spectral sensitizers of Example 5. To each sample of the emulsion is added the infrared sensitizer 3,3'-diethylselenadibocyanine ethylsulfate at 400 mg./silver mole, 4 g. of 4-hydroxy-6-methyl-1,3a,7-tetraazaindene/silver mole and 2.5 ml. of 6-methoxyquinoline/silver mole. The emulsions are coated and samples are exposed one-fifth second to blue and white light as described in Example 1 and to an exposure modulated by a Wratten 89B filter (infrared), processed in Kodak DK-50 Developer, fixed, washed and dried. The results are as follows:

Emulsion Preparation		Relative Speeds			Fog
		Blue	Clear	Infrared	
pH 2.0	pAg 8.8	100	257	148	.09
pH 5.6	pAg 8.8	16	71	30	.70

It is apparent that sensitization to the infrared region of sulfur- and gold-sensitized cubic-grained emulsions made at a pH of 5.6 causes heavy fog, whereas the same emulsion prepared at a pH of 2.0 is effectively sensitized to the infrared region.

The silver halide employed in the preparation of the cubic-grain emulsions of this invention includes any of the photographic silver halides as exemplified by silver bromide, silver chloride and silver iodide, or mixed silver halides such as silver chlorobromide or silver bromiodide, and the like. Particularly good results are obtained with silver halide emulsions in which the halide is predominantly bromide and the average grain size of the silver halide crystals is less than 0.5 micron.

Mean grain diameter, i.e., average grain size, can be determined using conventional methods, e.g., projective area and diameters of equivalent circles such as described in "Methods of Particle-Size Analysis," *ASTM Symposium on Light Microscopy*, by Loveland, 1953, pages 94-122, and as disclosed in Chapter 2 of "The Theory of the Photographic Process," by Mees and James, 1966, New York, The MacMillan Company.

Emulsion layers and other layers present in photographic elements made according to this invention can be hardened with any suitable hardener such as aldehyde hardeners, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxystarch, oxy plant gums, and the like.

The cubic-grain emulsions can also contain additional additives, particularly those known to be beneficial in photographic emulsions including, for example, stabilizers or antifoggants, particularly the water-soluble inorganic acid salts of cadmium, cobalt, manganese and zinc as disclosed in U.S. Pat. No. 2,829,404, the substituted triazaindolizines as disclosed in U.S. pat. Nos. 2,444,605 and 2,444,607, speed-increasing materials, plasticizers and the like. Sensitizers which give particularly good results in the photographic compositions disclosed herein are the alkylene oxide polymers which

can be employed alone or in combination with other materials, such as quaternary ammonium salts, as disclosed in U.S. Pat. No. 2,886,437, or with mercury compounds and nitrogen-containing compounds, as disclosed in U.S. Pat. No. 2,751,299.

The emulsions of this invention can be used in color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials.

The emulsions of the invention are especially useful in color photography particularly where spectral sensitizers are incorporated in the emulsions, in which case a color coupler will be incorporated to correspond to the spectral sensitivity which has been imparted.

The emulsions of this invention can be used in diffusion transfer processes which utilize the non-developed silver halide in the non-image areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott, U.S. Pat. No. 2,352,014; Land, U.S. Pat. No. 2,543,181; and Yackel et al., U.S. Pat. No. 3,020,155. The cubic silver halide emulsions described herein can also be used in color transfer processes which utilize the diffusion transfer of an imagewise distribution of developer, coupler or dye from a light-sensitive layer to a second layer while the two layers are in close proximity to one another. Color transfer processes of this type are described in Yutzy, U.S. Pat. No. 2,856,142; Land et al., U.S. Pat. No. 2,983,606; Whitmore et al., British pat. Nos. 904,364 and 840,731; and Whitmore et al., U.S. application Ser. No. 392,471. The cubic silver halide emulsions of this invention can be processed in monobath processes such as described in Haist et al., U.S. Pat. No. 2,875,048, or in stabilization-type processes.

Variable contrast in the cubic-grain emulsions can be obtained by exposing through various Kodak Wratten filters a spectrally sensitized cubic-grain emulsion, whereby the level of the sensitizing dye used is sufficient to cover at least 60 percent of the grain surface. Appropriate filters are described in Kodak pamphlet "Kodak Wratten Filters," data book B-3, 1965.

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A method of preparing silver halide grains of cubic-regular shape free of reduction sensitization which comprises running an aqueous solution of silver nitrate and an aqueous solution of water-soluble halide simultaneously into an agitated aqueous solution of a peptizer in a double-run precipitation procedure while maintaining the pH at no more than 4.0 and the pAg at a value within the range of 8.6 to 9.2.

2. A method according to claim 1 wherein said silver halide is silver bromiodide.

3. A method according to claim 1 wherein said silver halide grains are chemically sensitized with a compound containing a labile atom selected from the group consisting of sulfur, selenium and tellurium atoms.

4. A method according to claim 1 including the step of gold-sensitizing said silver halide grains.

5. A cubic-regular grain silver halide emulsion, said grains being substantially free of reduction sensitization upon formation, said silver halide being thereafter chemically sensitized with a compound containing a labile atom selected from the group consisting of sulfur, selenium and tellurium and spectrally sensitized with a dye having anodic half-wave potential less than 1.0 volt and a cathodic half-wave potential less than -0.8 volt.

6. A cubic-regular grain silver halide emulsion in which the halide is predominately bromide, said grains being substantially free of reduction sensitization upon formation, said silver halide being chemically sensitized with a compound

containing a labile atom selected from the group consisting of sulfur, selenium and tellurium, and spectrally sensitized with a cyanine dye having an anodic half-wave potential less than 1.0 volt and a cathodic half-wave potential less than -0.8 volt.

7. The emulsion of claim 6 in which the silver halide is silver bromiodide having an average grain diameter of less than 0.5 micron.

8. The emulsion of claim 6 additionally being gold-sensitized.

9. The emulsion of claim 6 wherein it is spectrally sensitized with a cyanine dye containing at least one heterocyclic ring selected from the class consisting of thiazole, benzimidazole, oxazole, selenazole and quinoline.

10. A silver halide emulsion according to claim 6 which has been sulfur- and gold-sensitized.

11. A silver halide emulsion according to claim 6 comprising an infrared-sensitizing dye.

12. An emulsion according to claim 6 wherein the average grain diameter of said silver halide is less than 0.5 micron.

13. An emulsion according to claim 6 wherein said grains are made at a pH of about 2.

14. An emulsion according to claim 6 wherein at least 80 percent, by weight or by number, of said silver halide grains are free of twin plane stacking faults.

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