United States Patent Office 3,375,114 Patented Mar. 26, 1968

3,375,114

HIGH EDGE GRADIENT SILVER HALIDE EMULSION

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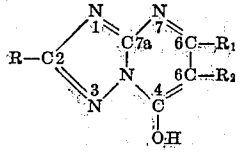
No Drawing. Filed Mar. 29, 1965, Ser. No. 443,662
Claims priority, application Japan, Dec. 26, 1961, 37/47,418
6 Claims. (Cl. 96—107)

This invention relates to a photographic emulsion of silver halide and more particularly to a photographic emulsion giving an image of high edge gradient.

The ratio of change in density to distance at the boundary between the darkened part and the undarkened part of a photographic image is called "edge gradient." In general, the higher the edge gradient, the sharper the image. In order to obtain an image of high edge gradient, a special developing solution which contains a small amount of sulfite salt, having a high pH value and containing hydroquinone alone as developer, has been employed (for example, ref. Yule, J.A.C., "Formaldehyde-Hydroquinone Developers and Infectious-Development," J. Frank, Inst., 239,221 (1945)).

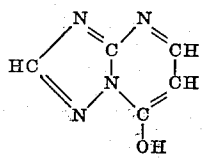
It is the object of this invention to provide a photographic emulsion which gives an image of high contrast when a developing solution of this type is employed.

Photosensitive materials using such emulsion are suitable for making the half-tone reproductions by means of reproduction screens such as glass screen and contact screen. The above-mentioned object can be attained by adding to the emulsion (1) the derivatives of 4-hydroxy-1,3,3a-7-tetrazaindene and (2) at least one compound selected from the group consisting of lysine and arginine and their salts. The derivatives of 4-hydroxy-1,3,3a,7-tetrazaindene are represented by the following structural formula:

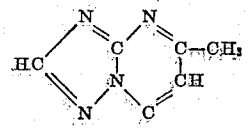


where R and R_1 represent hydrogen atom, alkyl group, aralkyl group or aryl group, and R_2 represents hydrogen atom, alkyl group, carboxy group or carboalkoxy group.

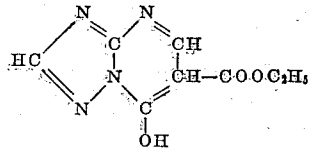
The derivatives of tetrazaindene capable of being employed in this invention can be synthetized by heating 1 mole of β-ketoesters, malonic esters of α-ethoxymethylene-β-ketoesters with 1 mole of 3-amino-1,2,4-triazoles. Examples of such tetrazaindene are as follows:

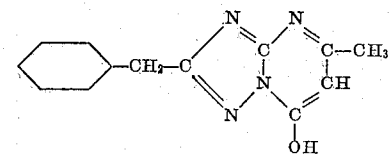


(I)



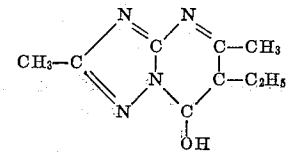
(II)

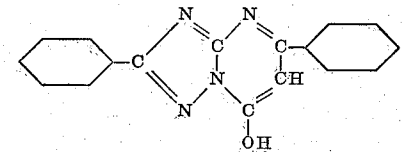


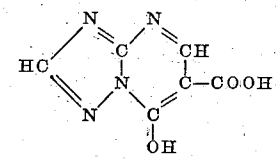


(IV)

Additional examples of tetrazaindenes are as follows:

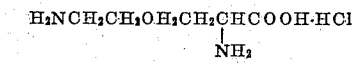






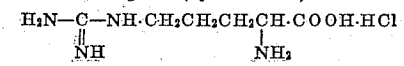
Lysine and arginine used in this invention are basic amino-acids, and both that prepared by the decomposition of proteins and that prepared by synthesis may be employed. These compounds are represented by the following structural formulae:

Lysine (hydrochloride)



(V)

Arginine (hydrochloride)



(VI)

The amount of compounds employed in this invention varies according to the sort of emulsion, but it is preferable to add 10 mg. to 1 g. of tetrazaindene, 0.1 g. to 10 g. of lysine or arginine or their salts per 1 mole of silver halide.

Photographic emulsions are prepared in the following three stages: (1) The emulsification and digestion (first ripening) of the silver halide, (2) removal of excess of salts by washing with water and the like, and (3) second digestion (after ripening) to increase the sensitivity. The compounds may be added at any stage. Tetrazaindene may be added either before or after the addition of lysine or arginine, but it is most preferable to add these substances after the second ripening and before coating. These substances are dissolved in the solvents that have no detrimental effect on the emulsion, for example, water, lower alcohols such as methanol and ethanol, and ketones, and then added to the emulsion.

In this invention an emulsion of silver chloride, silver bromide, silver chlorobromide, silver iodo bromide, or silver chloroiodo bromide may be employed, but that of silver chlorobromide is most preferable.

The emulsion may be chemically sensitized by unstable compounds containing sulfur, such as ammonium thio-

sulfate, and allyl thiourea (ref. P. Glafkide's Chimie Photographique, 2 éme Edition Photochinema, Paul Montel Paris 1957, pp. 297–299), and/or a compound of gold such as a complex of aurous compound and thiocyanic acid (ref. ibid, p. 301) according to the well-known method in the art. The emulsion may be optically sensitized by the addition of sensitizing dyes such as cyanine dyes or merocyanine dyes (for example, ref. Shinichi Kikuchi et al. "Handbook of Scientific Photograph" 1959, pp. 15–24, Maruzen Co.). The emulsion may contain a hardening agent such as chromium alum, formaldehyde, or others (ref. ibid. pp. 29–47). In order to facilitate the coating of emulsion, a surface-active agent may be added.

Tetrazaindenes have been well known as a stabilizer in the emulsion for negatives, but are employed in this invention to improve the contrast. When tetrazaindenes are used alone, the improvement of the halftone-dot due to the improvement of contrast, that is the increase of edge gradient, cannot be attained because of the decrease of developing rate. Satisfactory results can be obtained by using tetrazaindenes along with arginine or lysine.

In order to facilitate the understanding of this invention, examples will be given hereafter. It should be realized that this invention is not limited by examples but limited by the appended claims.

EXAMPLE 1

Four samples weer prepared by adding 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene (II) and/or hydrochloride of lysine (V) to the emulsion of silver chlorobromide which contains 30 mole percent of silver bromide, the optimum amounts of sensitizing dye and hardening agent, and gelatin in a proportion of 105 g. of gelatin to 1 mole of silver halide. The amounts of (II) and (V) were as follows:

Sample	G./l. mole of silver halide	
	(II)	(V)
(i)	0	[1] 0
(ii)	0.96	0
(iii)	0	4.09
(iv)	0.96	4.09

[1] Reference.

These samples were coated on film bases and dried. Then sensitometry and evaluation of halftone-dot were carried out using these test films.

Sensitometry was carried out in the following manner. A test film was exposed to light, emitted from a tungsten lamp (2666° K.) and passing through an optical step-wedge, and then developed at 20° C. in a developer of the following formula:

Water (about 30° C.)	cc	500
Sodium sulfite (anhydrate)	g	300
Para-formaldehyde	g	7.5
Sodium bisulfite	g	2.2
Boric acid	g	7.5
Hydroquinone	g	22.5
Potassium bromide	g	1.6
Additional water		Balance
Total	liters	1

The evaluation of halftone-dot was carried out in the following manner. A test film was closely contacted on a commercial magenta contact screen (150 lines) during exposure and then developed in the same way as in the case of sensitometry. The developed halftone-dot was observed by means of a microscope and classified into five classes A, B, C, D and E in accordance with the sharpness of edge of dot. The results of development of 1'30", 2'15" and 3' at 20° C. are listed in the following table.

Sample	Relative sensitivity			Contrast*			Sharpness of dot		
	1'30"	2'15"	3'	1'30"	2'15"	3'	1'30"	2'15"	3'
(i)	25	63	100	4.0	7.3	7.0	D	B	C
(ii)	12	23	65	2.7	5.5	7.5	E	C	A
(iii)	58	79	103	7.7	6.9	6.2	A	C	D
(iv)	35	70	97	6.1	8.1	7.2	B	A	B

*Average slope between base density+fog density+0.1 and base density+fog density+2.1.

As seen from this table, Sample iv provides sharp dots of high contrast in a wide range of time of development.

EXAMPLE 2

As in Example 1, four samples were prepared by adding 5-carboxy-4-hydroxy-1,3,3a,7-tetrazaindene (II) and/or hydrochloric salt of arginine (VI) to the emulsion. The amounts of (II) and (VI) per 1 mole of silver halide were as follows:

Sample	G./l. mole of silver halide	
	(II)	(VI)
(i)	0	[1] 0
(ii)	0.24	0
(iii)	0	1.9
(iv)	0.24	1.9

[1] Reference.

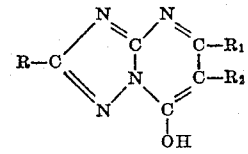
Results of tests are summarized in the following table:

Sample	Relative sensitivity			Contrast			Sharpness of dot		
	1'30"	2'15"	3'	1'30"	2'15"	3'	1'30"	2'15"	3'
(i)	25	63	100	4.0	7.3	7.0	D	B	C
(ii)	11	20	55	2.3	4.9	7.5	E	C	A
(iii)	77	90	103	7.3	5.7	5.4	A	C	D
(iv)	25	57	85	4.2	7.7	8.1	B	A	A

As seen from this table, (iv) provides sharp dots of high contrast in a wide range of time of development.

What is claimed is:

1. A photographic emulsion of silver halide characterized in that in order to increase the edge gradient of image the said emulsion contains (1) at least one compound selected from the group consisting of 4-hydroxy-1,3,3a,7-tetrazaindenes which are represented by the following structural formula:



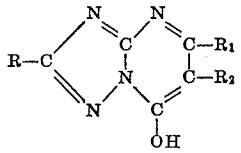
in which R and R_1 represent a member selected from the group consisting of hydrogen atom and alkyl groups and R_2 represents a member selected from the group consisting of hydrogen atom, alkyl groups, carboxy groups, and carboalkyl groups, and (2) at least one compound selected from the group consisting of lysine, arginine and their salts.

2. A photographic emulsion according to claim 1 wherein said compound (2) is lysine hydrochloride.

3. A photographic emulsion according to claim 1 wherein said compound (2) is arginine hydrochloride.

4. A method of increasing the edge gradient of image of silver halide photographic emulsion comprising adding thereto (1) at least one compound selected from the group

consisting of 4-hydroxy-1,3,3a,7-tetrazaindenes which are represented by the following structural formula:



in which R and R_1 represent a member selected from the group consisting of hydrogen atom and alkyl groups and R_2 represents a member selected from the group consisting of hydrogen atom, alkyl groups, carboxy groups, and carboalkoxy groups, and (2) at least one compound selected from the group consisting of lysine, arginine and their salts.

5. A method according to claim 4 wherein said compound (2) is lysine hydrochloride.

6. A method according to claim 4 wherein said compound (2) is arginine hydrochloride.

References Cited

UNITED STATES PATENTS

2,944,902 7/1960 Carroll et al. ---------- 96—107

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G. COHN, *Assistant Examiner.*