

1

3,369,905

PHOTOGRAPHIC SILVER HALIDE EMULSIONS CONTAINING POLYAMINE SENSITIZING AGENTS

Jean E. Jones and Charles V. Wilson, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey
No Drawing. Filed Mar. 19, 1963, Ser. No. 266,192
11 Claims. (Cl. 96-107)

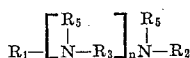
This invention relates to photography and particularly to sensitizers for photosensitive colloid-silver halide emulsion layers.

Polyalkyleneimino compounds (polyamines) having primary amino end groups are described for use as chemical sensitizers for photographic silver halide emulsions in U.S. Patents No. 2,743,182, patented Apr. 24, 1956, and No. 2,518,698, patented Aug. 15, 1950. Many of these chemical sensitizers increase speed of photographic emulsions but have the disadvantage of substantially increasing fog in the emulsions, especially in emulsions sensitized with sulfur and gold.

An object of the present invention is to provide novel photographic colloid-silver halide emulsions containing a polyamine sensitizing agent which will increase the speed of the emulsion with only very slight or no increase in fog, even in emulsions sensitized with sulfur and gold.

This and other objects of the invention are obtained by incorporating into a photographic colloid-silver halide emulsion a polyalkyleneimino compound having at least one secondary or tertiary amino end group. Even better results are obtained when all of the nitrogen atoms in the polyamine chain are fully substituted. Effective amounts of sensitizer in the emulsion are usually in the range from 0.03 to 5.0 grams sensitizer per mole silver.

Polyalkyleneimino compounds that are useful as sensitizers according to the present invention have the formula:



wherein each of R_1 and R_5 represents a member selected from the group consisting of hydrogen, alkyl containing 1-4 carbon atoms, hydroxyalkyl, aryl, aralkyl, alkyl substituted aryl and alkoxy substituted aryl; R_2 represents a member selected from the group consisting of alkyl containing 1-4 carbon atoms, hydroxyalkyl, aryl, aralkyl, alkyl substituted aryl and alkoxy substituted aryl; each R_3 is an alkylene chain having from 2-3 carbon atoms in the chain with each of said carbon atoms having attached thereto members selected from the group consisting of hydrogen, alkyl containing 1-4 carbon atoms, aryl of 6-10 carbon atoms and aralkyl, the alkyl group in each said aralkyl being of 1-2 carbon atoms; n is a positive whole integer from 1-3 and the radical

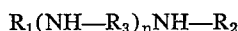


is a unit in the linear chain of the polyamine.

Specific examples of compounds having the above formula are:

- (1) N,N'-di-beta-hydroxyethylethylenediamine
- (2) 8-amino-3,6-diazoctanol
- (3) 3,6,9-triaza-1,11-undecanediol
- (4) 3,6,9-trimethyltriaza-1,11-undecanediol
- (5) 4,15-diazoctadecane-1,18-bisdimethylamine

Compounds 1 and 3 in the above list may be represented by the formula:



wherein R_1 and R_2 are members selected from the group consisting of alkyl containing 1-4 carbon atoms, hydroxy

2

alkyl, aryl, aralkyl, alkyl substituted aryl and alkoxy substituted aryl, R_3 is an alkylene chain having from 2-3 carbon atoms in the chain with each of said carbon atoms having attached thereto members selected from the group consisting of hydrogen, alkyl containing 1-4 carbon atoms, aryl of 6-10 atoms and aralkyl, the alkyl group in said aralkyl being of 1-2 carbon atoms, and n is a positive whole integer from 1-3 and the radical NHR_3 is a unit in the linear chain of the polyamine.

Additional specific examples of compounds having the last formula above are:

- (6) N,N''-dimethyltriethylenetetramine
- (7) N,N''-dimethyldiethylenetriamine
- (8) N,N'-dimethylethylenediamine
- (9) N,N'-dibenzylethylenediamine
- (10) N,N'-di-n-butylethylenediamine
- (11) N,N'-dimethyltrimethylenediamine
- (12) N,N'-dimethyl-1,2-propanediamine
- (13) N,N'-diphenylethylenediamine

The invention may be better understood by reference to the following examples which describe in detail some preferred embodiments of the invention.

Example I

Conventional fast silver bromide-gelatin emulsions, chemically sensitized with sulfur and gold compounds and spectrally sensitized with cyanine dyes were prepared by conventional procedures and each of the compounds numbered 1-5 above was added respectively to a separate sample of emulsion in the concentrations shown in Table 1. Control samples of each emulsion were also kept. The sensitized and control emulsion samples were coated by conventional melt coating procedures on cellulose acetate film, then chill-set and dried. Respective samples of the film were exposed on an Eastman sensitometer Type IB to light of daylight quality for $\frac{1}{25}$ second and were developed for 5 minutes in Kodak Developer DK-50 at 68° F., then fixed and dried. Relative speed was determined at the exposure necessary to produce density of 0.2 above fog. Results of the tests in terms of relative speed, gamma and fog are tabulated in Table 1.

TABLE 1

Emulsion	Sensitizing Compound (by number as above) and Concentration in Grams Per Mole Silver	Relative Speed	Gamma	Fog Density
A.....	Control.....	100	1.07	.16
A.....	1. (0.03).....	97	1.09	.15
A.....	1. (0.3).....	117	1.14	.17
A.....	1. (3.0).....	150	1.15	.22
B.....	Control.....	100	1.46	.11
B.....	2. (0.30).....	110	1.14	.13
C.....	Control.....	100	1.07	.10
C.....	3. (0.30).....	159	1.03	0.10
C.....	4. (0.30).....	118	1.04	0.08
D.....	Control.....	100	1.80	.12
D.....	5. (0.30).....	125	1.50	.13

Data in Table 1 show results obtained using different sensitizers of the class described at concentrations from 0.03 to 3.0 grams per mole silver in the emulsion. Optimum results were obtained at concentrations in the magnitude of 0.3 gram per mole, however, the sensitizing effect was appreciable at other concentrations.

Variations from the colloid-silver halide emulsion compositions described in the examples herein may be made within the scope of the present invention. The class of sensitizers defined above are effective to increase speed in a wide variety of photosensitive silver halide emulsions familiar to those skilled in the art. The invention includes photographic emulsions made from suitable colloids other than gelatin and containing other functional addenda as will be familiar to emulsion makers.

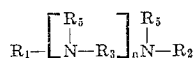
The invention has been described with reference to cer-

3

tain preferred embodiments but it will be understood that variations and modifications of the invention as described can be made within the scope of the invention as defined in the following claims.

We claim:

1. A colloid-silver halide photographic emulsion containing at least one linear polyamine sensitizing agent having the formula:

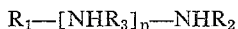


wherein each of R_1 and R_5 represents a member selected from the group consisting of hydrogen, alkyl containing 1-4 carbon atoms, hydroxyalkyl, aryl, aralkyl, alkyl substituted aryl and alkoxy substituted aryl; R_2 represents a member selected from the group consisting of alkyl containing 1-4 carbon atoms, hydroxyalkyl, aryl, aralkyl, alkyl substituted aryl and alkoxy substituted aryl; each R_3 is an alkylene chain having from 2-3 carbon atoms in the chain with each of said carbon atoms having attached thereto members selected from the group consisting of hydrogen, alkyl containing 1-4 carbon atoms, aryl of 6-10 carbon atoms and aralkyl, the alkyl group in each said aralkyl being of 1-2 carbon atoms; n is a positive whole integer from 1-3 and the radical



is a unit in the linear chain of the polyamine.

2. A colloid-silver halide photographic emulsion containing at least one linear polyamine sensitizing agent having the general formula:



wherein R_1 and R_2 are selected from the group consisting of alkyl of 1 to 4 carbon atoms, aryl, aralkyl, hydroxy substituted alkyl and alkyl substituted aryl and alkoxy substituted aryl; R_3 is an alkylene chain having from 2 to 3 carbon atoms in the chain with each of said carbon atoms having attached thereto members selected from the group consisting of hydrogen, alkyl of 1 to 4 carbon atoms, aryl of 6 to 10 carbon atoms and aralkyl, the alkyl group in said aralkyl being of 1 to 2 carbon atoms; and n is a positive whole number from 1 to 3 and the radical, NHR_3 is a unit in the linear chain of the polyamine.

4

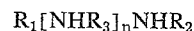
3. An emulsion as set forth in claim 2 wherein said colloid is gelatin.

4. A colloid-silver halide photographic emulsion containing a linear amine sensitizing agent having the formula:



wherein R_1 is selected from the group consisting of an alkyl radical of 1 to 4 carbon atoms and hydroxy substituted alkyl and R_3 is an alkylene chain having 2 to 3 carbon atoms in the chain with each of said carbon atoms having attached thereto members selected from the group consisting of hydrogen and an alkyl of 1 to 4 carbon atoms.

5. A colloid-silver halide photographic emulsion containing at least one linear polyamine sensitizing agent having the formula:



wherein R_1 and R_2 are hydroxy substituted alkyl, R_3 is an alkylene chain having 2 carbon atoms, n is a positive whole integer from 1 to 2, and the radical NHR_2 is a unit of the linear chain of the polyamine.

6. An emulsion as defined in claim 5 wherein said colloid is gelatin.

7. An emulsion as defined in claim 2 wherein said sensitizing agent is *N,N*-di-beta-hydroxyethylethylenediamine.

8. An emulsion as defined in claim 1 wherein said sensitizing agent is 8-amino-3,6-diazaoctanol.

9. An emulsion as defined in claim 2 wherein said sensitizing agent is 3,6,9-triaza-1,11-undecanediol.

10. An emulsion as defined in claim 1 wherein said sensitizing agent is 3,6,9-trimethyltriaza-1,11-undecanediol.

11. A colloid-silver halide photographic emulsion containing 4,15-diazaoctadecane - 1,18 - bisdimethylamine as a linear polyamine sensitizing agent.

References Cited

UNITED STATES PATENTS

3,026,203	3/1962	Chamber et al.	96-107
2,016,471	10/1935	Wilmanns et al.	96-107
2,518,698	8/1950	Lowe et al.	96-107

NORMAN G. TORCHIN, *Primary Examiner*.

J. T. BROWN, *Assistant Examiner*.