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2,756,145

SILVER HALIDE EMULSIONS CONTAINING A DI-AMINO DIPHENYL AMINE STABILIZER

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No Drawing. Application December 31, 1953,
Serial No. 401,718

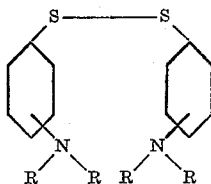
5 Claims. (Cl. 95—7)

Our invention relates to the stabilization of light sensitive silver bromide emulsions such as silver bromide-gelatin emulsions.

It is known that silver bromide emulsions such as are used to sensitize photographic papers lose their sensitivity upon storage of the photographic paper sensitized therewith.

One object of our invention is to provide emulsions which retain their sensitivity much more effectively when photographic products sensitized by said emulsions are stored. Other objects of our invention will appear herein.

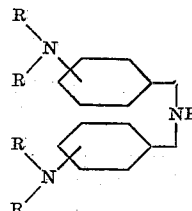
We have found that the stability of silver bromide emulsion layers is markedly improved if there is incorporated into the emulsion, prior to the coating therewith of a support, an ortho or para diaminodiphenyldisulfide or its salt or an ortho or para diaminodiphenyl amine or its salt. The stabilization of the emulsion is effective with either the unsubstituted compounds or with compounds in which dimethyl or diethyl amino groups are used. Some of the compounds which have been found to be useful for stabilizing silver bromide emulsions in accordance with our invention are 4,4'-diaminodiphenyldisulfide dihydrochloride, 2,2'-diaminodiphenyldisulfide, 4,4'-diaminodiphenyl amine sulfate, 4,4'-dimethylamino diphenylamine hydrochloride, and the like. We have found that various proportions of the amines or disulfides as specified are useful for stabilizing silver bromide emulsions but that more effective results are obtained if the amount of the compound added to the emulsion is equivalent to at least 2 mg. per mole of silver halide. The proportion of 2-32 mg. of the disulfide or amine per mole of silver halide has been found to be the most successful. Those disulfides which appear to be most useful in accordance with our invention are those having the formula as follows:



where the amino groups are either ortho or para to the sulfide substituent, R being selected from the group consisting of hydrogen, methyl and ethyl. In the above formula either R may be the same in any one compound, some of the R's may be different than the others or the R's may all represent different substituents. As for the

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amines which are useful the following structural formula illustrates compounds which may be employed:



where R may be either hydrogen, methyl or ethyl; R may be either all the same or some may be hydrogen and others may be methyl or ethyl groups. If desired these compounds may be employed in the form of their salts such as the hydrochloride or the sulfate.

The amount of the additive employed in the silver bromide emulsion may be any amount thereof from 2 up to 32 mg. per mole of silver halide in the emulsion. The emulsions which are stabilized in accordance with our invention are characterized by the use of silver bromide as the principal sensitizing material but there may be cases where some other silver halide may be employed. Although our invention is primarily directed to the stabilizing of gelatin photographic emulsions, we are also aware that there may be some other suspending material substituted at least in part for the gelatin of the photographic composition. The carrying material for the silver bromide may be polyvinyl alcohol, may be a modified protein as described in Lowe and Gates Patent No. 2,691,582 issued October 12, 1954, or some other protein material, or may be a synthetic polymer material, or it may be a mixture of gelatin with some other protein material or a polymeric hydrosol such as disclosed in application Serial No. 272,709 of Fowler or in the applications relating to polymers prepared from protein derivatives and their mixtures with gelatin, in the names of Fowler and Gates and Gates, Illingsworth and Dann, Serial Nos. 398,234 and 398,236 respectively, filed December 14, 1953.

The following examples illustrate our invention:

EXAMPLE 1

A silver bromide emulsion containing 1.3 mol percent silver iodide was divided into several fractions and to each fraction was added 4,4'-diaminodiphenyldisulfide dihydrochloride in various proportions from 2 to 32 mgs. per mole of silver halide. Each emulsion fraction was applied as a thin layer on to baryta coated paper base. A sample of each coating was used for preparing a paper test strip. Each test strip was then exposed on a sensitometer and developed for one minute in photographic developer, D-72, diluted 1:1. The strips were then read on a densitometer and contrast measurements were made to determine the value of log ES obtained in the manner described. This value indicates the change in contrast of the paper over a period of time. The larger the degree of difference as indicated by log ES the greater the amount of breakdown which has occurred. (See page 189 of "Fundamentals of Photographic Theory"—James and Higgins.)

After the above procedure the test strips were read on a densitometer and contrast measurements were made as described. The value of log ES was obtained in accord-

ance with the method specified by the American Standard for Sensitometry of Photographic Papers Z38.2.3. Other samples of the same coatings were incubated for 4 days at 120° F. and 35% relative humidity and were exposed, developed, and measured for contrast in the same way as the freshly coated samples. The following table indicates the results, column 1 indicating the milligrams of 4,4'-diaminodiphenyldisulfide dihydrochloride added per mole of silver halide. Column 4 indicates the differences between the log ES values of incubated and fresh strips. 10

Table 1

(1) Mg.	(2) Fresh Log ES	(3) Incub. Log ES	(4) Δ Log ES
0.....	.71	1.31	.60
2.....	.58	1.00	.42
4.....	.59	.92	.33
8.....	.64	.82	.18
16.....	.64	.89	.25
32.....	.71	1.00	.29

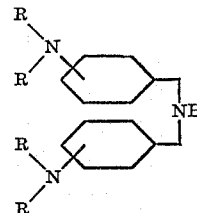
EXAMPLE 2

A silver bromide emulsion having different sensitometric characteristics than that of the emulsion employed in the previous example was divided into several fractions. There was added an amount of a stabilizer in accordance with our invention equivalent to 2 mgs. per mole of silver bromide in the emulsion. The various fractions were tested while fresh and after 4 days incubation in the manner described in the previous example. The values given show the change in log ES as a result of the incubation:

Added stabilizer:	Δ log ES
2,2-diaminodiphenyldisulfide	.00
4,4'-diaminodiphenylamine sulfate.....	.06
4,4'-dimethylamino diphenylamine hydrochloride	-.04
2,2'-dimethylamino diphenyl disulfide.....	.01

We claim:

1. A silver halide photosensitive emulsion stabilized against deterioration by aging, which emulsion contains 2-32 mgs. per mole of silver halide of a compound selected from the group consisting of the diaminodiphenyl amines having the structural formula:



the R substituent being selected from the group consisting of hydrogen, methyl, and ethyl, and the mineral salts thereof.

2. A silver bromide photosensitive emulsion stabilized against deterioration by ageing which emulsion contains 2-32 mgs. per mole of silver halide of a diaminodiphenyl amine.

3. A silver bromide photosensitive emulsion stabilized against deterioration by ageing which emulsion contains 2-32 mgs. per mole of silver halide of a diaminodiphenyl amine salt.

4. A photosensitive silver bromide emulsion which emulsion is stabilized against deterioration due to ageing by a content of 2-32 mgs., per mole of silver halide, of 4,4'-dimethylaminodiphenyl amine hydrochloride.

5. A photosensitive silver bromide emulsion which emulsion is stabilized against deterioration due to ageing by a content of 2-32 mgs. per mole of silver halide of 4,4'-diaminodiphenyl amine sulfate.

References Cited in the file of this patent

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