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2,828,203

## METHOD OF INCREASING CLAYDEN DESENSITIZATION OF PHOTOGRAPHIC EMULSIONS

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This invention relates to photography and particularly to a method of increasing the susceptibility of silver halide emulsions to Clayden desensitization.

It has been shown that the sensitivity of some photographic materials when exposed by a relatively long duration exposure may be reduced if the materials have first been exposed to illumination of short duration, i. e. 0.001 second or less. This effect has been called the Clayden effect. The feature which characterizes the Clayden effect is that the initial exposure of short duration to relatively high intensity light desensitizes the emulsion so that subsequent exposure to weak intensity light produces less effect than if the pre-exposure had not been given. As usually observed, the density resulting from the two superposed exposures is less than that of the single exposure to the low intensity light.

The effect known as the Clayden effect has a number of practical applications. Yule and Maurer have described in their U. S. Patent 2,691,586 use of the Clayden effect in preparing a pre-screened photographic material with which halftone negatives may be prepared from a continuous tone original without the use of the conventional halftone screen. The usefulness of such pre-screened materials in the graphic arts for letterpress, lithographic and intaglio printing depends on the degree of desensitization obtainable and hence, on the degree of sensitivity of the material to the Clayden effect.

Frequently the Clayden effect desensitization produced in an emulsion is not sufficiently great to give a commercially useful result. It is therefore the principal object of my invention to provide a novel method of increasing the susceptibility of the emulsion to Clayden desensitization. Other objects will appear from the following description of my invention.

These objects are accomplished by incorporating in a silver halide emulsion which shows at least some susceptibility to Clayden desensitization, a merocyanine or hemioxonol dye of the class hereinafter defined.

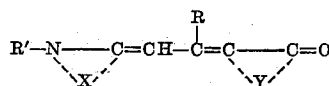
The emulsions which I use are those which initially, that is, without merocyanine or hemioxonol dye, are Clayden desensitizable to some degree and by the addition of these dyes become Clayden desensitizable to a useful degree. By "Clayden desensitizable to some degree," I mean that a silver halide emulsion is used which when exposed under a step tablet having 28 steps starting with approximately zero density and increasing in intervals of 0.3 density, to light from a high intensity flash lamp having 18,000 lumen seconds output in .0005 second, two feet from the emulsion, and without intermediate treatment is again exposed with the step tablet rotated 90°, to light from a 1000 watt tungsten lamp two feet from the emulsion, for two minutes, shows at least 0.10 log E or 1/3 step decrease in density between an area receiving only low intensity exposure and an area receiving the same level of low intensity exposure plus some level of high intensity exposure, when developed

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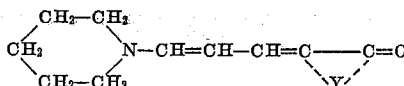
for 2 1/4 minutes at 68° F. in a developer of the following composition:

	Grams
Hydroquinone	22.2
Sodium sulfite, desiccated	30
Paraformaldehyde	7.5
Potassium metabisulfite	2.6
Boric acid, crystals	7.5
Potassium bromide	1.6
Water to 1 liter.	

According to my invention I add to a suitable emulsion at any stage before coating a merocyanine or hemioxonol dye having one of the following formulas



or



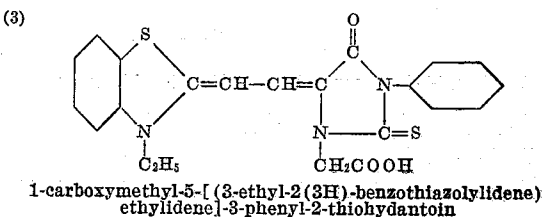
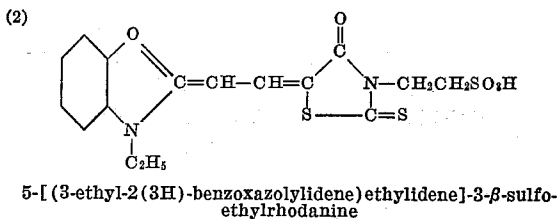
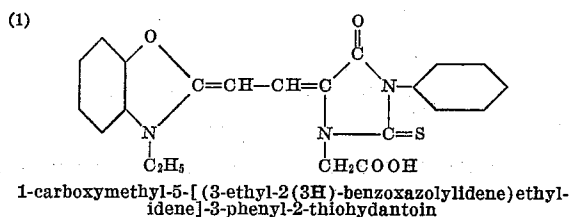
where X represents the atoms necessary to complete one of the following nuclei:

Thiazole  
Thiazoline  
Benzothiazole  
Naphthothiazole  
Benzoxazole  
Naphthoxazole  
Quinoline

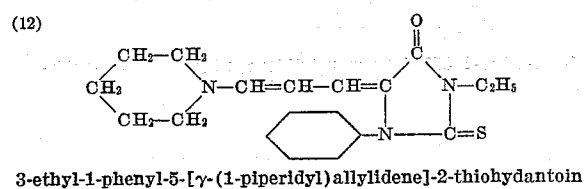
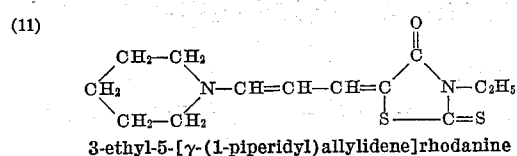
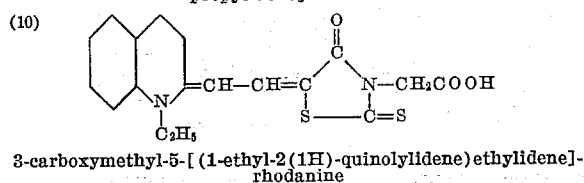
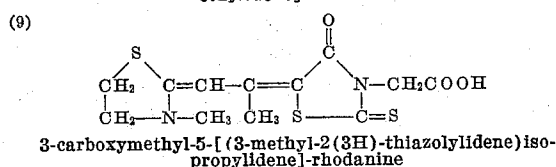
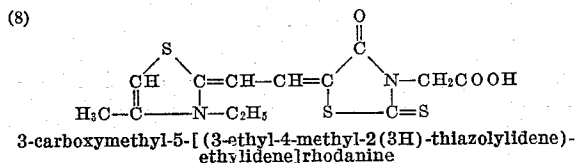
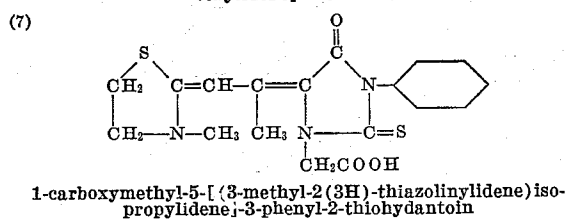
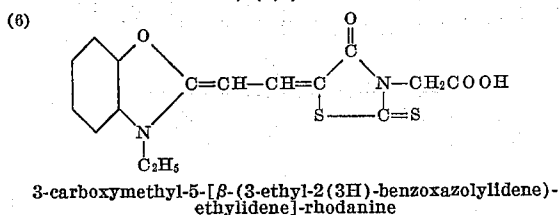
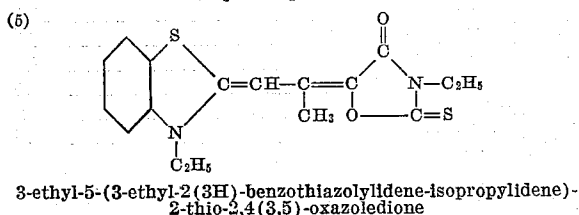
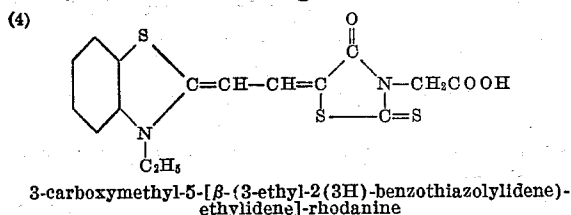
R represents hydrogen or an alkyl radical, e. g., methyl or ethyl, Y represents the atoms necessary to complete one of the following nuclei:

Rhodanine  
Thiohydantoin  
2-thioxazolidione

and R' represents an alkyl radical, e. g., methyl or ethyl. The following dyes may be used according to my invention:



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Compounds 1 to 4 and 6 to 10 are prepared as described in Brooker and Keyes U. S. Patent 2,493,748. Compound 1 is Example 15a, compound 2 is Example 11, compound 4 is Example 9, compound 6 is Example 10

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and compound 9 is Example 15b of that patent. Compound 5 is prepared as described in Brooker and White U. S. Patent 2,165,338, being Example 7 of that patent. Compounds 11 and 12 are prepared as described in Keyes U. S. Patent 2,186,608.

My invention will be further illustrated by reference to the following examples:

#### Example 1

- 10 To portions of a gelatino-silver halide emulsion which showed minimum Clayden effect when coated without sensitizing dye, there was added increasing amounts of 1 - carboxymethyl - 5 - [(3 - ethyl - 2(3H) - benzoxazolylidene) - ethylidene] - 3 - phenyl - 2 - thiohydantoin.
- 15 The separate emulsions were coated on film support, dried and preflashed to a short duration (.0001 second) exposure to a high intensity flash lamp of approximately 18,000 lumen seconds output, followed by an intensity scale exposure of 30 seconds duration to light from a 20 1000 watt tungsten lamp two feet from the emulsion. The test strips were developed 2½ minutes at 68° F. in the developer listed above, and the sensitivity decrease was determined in each of the samples with the following result:

	Amount of Dye, mg./mole Ag halide	Desensitization (Δ log E)
A	0	0.32
	50	0.32
	100	0.43
	150	0.88
B	0	0.14
	100	0.69
	133	1.22
	166	>1.60

This shows that the use of sensitizing dyes in the emulsion according to my invention provides a useful increase in the degree of desensitization which can be obtained.

#### Example 2

- A coating was made and treated as in Example 1, but using as the sensitizing dye 1-carboxymethyl-5-[(3-methyl - 2(3H) - thiazolylidene)isopropylidene] - 3-phenyl-2-thiohydantoin. The following results were obtained:

Amount of dye, mg./mole Ag halide	Desensitization (Δ log E)
0	0.32
50	0.19
100	0.53
150	1.60

#### Example 3

- A coating was made as in Example 1 containing 0.2 g. of the sensitizing dye per mole of silver, dissolved in methyl amine and alcohol. This coating was exposed by contact through a positive transparency to light from a Kodatron flash lamp (high intensity electronic flash of duration about 0.0001 second) at 2 feet. It was then given a general exposure to a 40 watt incandescent bulb at 5 feet for 20 seconds. The film was developed for 20 seconds in a developer of the following composition and a positive copy resulted.

	Grams
70 N-methyl-p-aminophenol sulfate	2.2
Hydroquinone	9
Sodium sulfite (desiccated)	96
Sodium carbonate (desiccated)	48
Potassium bromide	5
75 Water to 1 liter.	

## Example 4

A series of coatings was made as in Example 1, containing the indicated amounts of the following sensitizing dyes per mole of silver halide. When exposed and processed as in Example 1, the following results were obtained:

Dye	mg. Dye/mole Ag Halide	Desens. Log E Measured at a Density of 1.0
No dye.....		0.65
1 - Carboxymethyl - 5 - [(3 - ethyl - 2(3H) - benzoxazolylidene) - ethylidene] - 3 - phenyl - 2 - thiohydantoin.....	75	0.75
Do.....	150	1.10
3 - Carboxymethyl - 5 - [ $\beta$ - (3 - ethyl - 2(3H) - benzoxazolylidene) - ethylidene]rhodanine.....	75	0.55
Do.....	150	>2.30
3 - Carboxymethyl - 5 - [(3 - methyl - 2(3H) - thiazolylidene)iso-propylidene]rhodanine.....	75	0.32
Do.....	150	>2.50

The emulsions which I have prepared, while intended to produce a positive reproduction of the subject by means of the Clayden effect as described in the above examples, may also be used to produce a negative image by exposure either to the high intensity light source or to a low intensity light source but not both, and development in the customary manner. The composition of the developing solution is not critical (as long as the emulsion has the required properties, that is, is Clayden desensitizable) and my results may even be obtained with color developers containing the customary coupling or color-forming components.

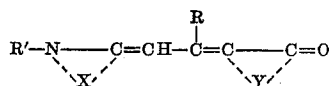
It will be understood that the examples included herein are illustrative only and that my invention is to be taken as limited only by the scope of the appended claims.

I claim:

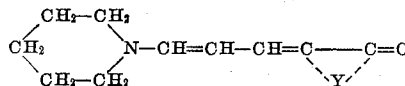
1. The method of obtaining a direct-positive image in a silver halide emulsion layer, which comprises imagewise exposing to a high intensity short duration flash of sufficient intensity and sufficiently short duration to produce a Clayden desensitization a silver halide emulsion which when exposed under a step tablet having 28 steps starting with approximately zero density and increasing in intervals of 0.3 density, to a light from a high intensity flash lamp having 18,000 lumen seconds output in .0005 second, two feet from the emulsion, and again exposed with the step tablet rotated 90°, to low intensity light from a 1000 watt tungsten lamp 2 feet from the emulsion for 2 minutes, shows at least 0.10 log *E* decrease in density between an area receiving only low intensity exposure and an area receiving the same level of low intensity exposure plus some level of high intensity exposure, when developed for 2¼ minutes at 68° F. in a developer of the following composition:

	Grams
Hydroquinone .....	22.2
Sodium sulfite, desiccated.....	30
Paraformaldehyde .....	7.5
Potassium metabisulfite.....	2.6
Boric acid, crystals.....	7.5
Potassium bromide .....	1.6
Water to 1 liter.	

said emulsion containing an appreciable amount of a dye selected from dyes having the general formulas:



and



where X represents the atoms necessary to complete a nucleus selected from the class consisting of thiazole, thiazoline, benzothiazole, naphthothiazole, benzoxazole, naphthoxazole and quinoline, R is selected from the class consisting of hydrogen and alkyl radicals, R' is an alkyl radical, and Y represents the atoms necessary to complete a nucleus selected from the class consisting of rhodanine, thiohydantoin and 2-thio-oxazolidinedione nuclei, then uniformly exposing said emulsion layer to a light source of sufficiently low intensity and for a sufficiently long time to produce a developable density in regions of said emulsion that received no high intensity exposure, and developing a positive image in said emulsion layer with a silver halide developing agent.

2. The method of claim 1, in which the dye is 1-carboxymethyl - 5 - [(3 - ethyl - 2(3H) - benzoxazolylidene)ethylidene]-3-phenyl-2-thiohydantoin.

3. The method of claim 1, in which the dye is 3-carboxymethyl - 5 - [ $\beta$  - (3 - ethyl - 2(3H) - benzoxazolylidene)ethylidene]-rhodanine.

4. The method of claim 1, in which the dye is 1-carboxymethyl - 5 - [(3 - methyl - 2(3H) - thiazolylidene)isopropylidene]-3-phenyl-2-thiohydantoin.

5. The method of claim 1, in which the dye is 3-carboxymethyl - 5 - [(3 - methyl - 2(3H) - thiazolylidene)isopropylidene]-rhodanine.

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