# United States Patent Office

## 3,044,874 Patented July 17, 1962

1

3,044,874 PHOTOGRAPHIC MATERIALS Stanley P. Popeck and Fritz Dersch, Binghamton, and William A. Wurth, Jr., Johnson City, N.Y., assignors to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware Filed Feb. 19, 1959, Ser. No. 794,252 No Drawing.

4 Claims. (Cl. 96-67)

This invention relates to photographic materials. More 10 particularly, this invention relates to photographic materials sensitized by means of water-soluble polyoxyethoxylated glycerol ricinoleates.

It is well known that the polyalkylene oxides such as the polyoxyethylenes and polyoxypropylenes, etc. in- 15 crease the speed of silver halide emulsions. This is disclosed in U.S. Patents Nos. 2,423,549 and 2,441,389. It is also known that certain condensation products of these polyalkylene oxides can be used to sensitize silver halide emulsions. Thus, U.S. Patent No. 2,240,472 and British 20 in which -CO-Ric-OH represents the ricinoleic acid Patent No. 443,559 disclose the use of condensation products of alkylene oxide with glycols such as those having from 8 to 18 carbon atoms. U.S. Patent No. 2,400,532 discloses the use of condensation products of alkylene oxides with hexitol ring dehydration products 25 as sensitizers. Condensation products of alkylene oxides with aliphatic amines, polyalkylene ethers, esters, and amides, the preparation of which is disclosed in U.S. Patent No. 1,970,578 have also been used as sensitizers. The polyalkylene oxide or derivative thereof used as a 30 sensitizer should have a molecular weight of at least 300 and preferably 1500 to 4000 or more.

The use of the polyalkylene oxides or their condensation products as sensitizers is limited because of their tendency to increase the formation of fog during storage 35 of the photographic film, especially storage at elevated temperatures and humidities. The use of conventional antifoggants is not sufficient to satisfactorily eliminate or minimize fog formation in a film coated with an emulsion containing a polyalkylene oxide or a condensation 40 product thereof as a sensitizer. Special antifoggants had to be found for use with such emulsions. The use of such special antifoggants is disclosed in U.S. Patents Nos. 2,704,716, 2,716,062 and 2,728,666.

It is an object of this invention to provide a novel  $^{45}$ sensitizer for use with a photographic emulsion to greatly increase the speed of the emulsion without materially increasing the fogging tendency thereof whereby any tendency of the emulsion to fog may be eliminated or 50minimized by the use of conventional antifoggants.

A further object of this invention is to provide a photographic film having a layer thereon containing a watersoluble polyoxyethoxylated glycerol ricinoleate.

Other objects and advantages of this invention will 55 appear to those skilled in the art from the detailed description thereof given below.

We have found that the water-soluble polyoxyethoxylated glycerol ricinoleates have a remarkable speed increasing effect on silver halide emulsions. Photographic emulsions containing water-soluble polyoxyethoxylated glycerol ricinoleates having a molecular weight of at least 1372 show an increase of density for a given exposure. We have also found that the polyoxyethoxylated glycerol ricinoleates do not have the objectionable tendency of increasing the fogging of photographic film during storage, especially storage under high temperature and humidity conditions. Fogging of photographic film having a coating of a silver halide emulsion and containing the novel sensitizer of our invention may, therefore, be controlled by the conventional antifoggants and stabilizers used in the photographic art and the use of a special type of antifoggant to prevent fogging of an

2

emulsion containing polyoxyalkylenes such as those disclosed in U.S. Patents Nos. 2,704,716, 2,716,062 and 2,728,666 becomes unnecessary.

U.S. Patent 1,970,578 discloses the preparation of polyoxyalkylene. The general formula for polyethylene oxide 5 or polyethylene glycol is:

### HOCH<sub>2</sub>CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>CH<sub>2</sub>CH<sub>2</sub>OH

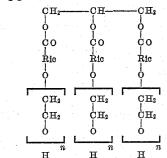
The formula for ricinoleic acid, a hydroxy derivative of oreic acid, is:

CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CH(OH)CH<sub>2</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>COOH A simplified formula of glycerol ricinoleate is:

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Ric	Ric 	Ric 
ÓН	DE	OH

group.

The hydroxy groups give rise to a reaction with ethylene oxide, thus forming polyethylene oxide derivatives of the following general formula:



The value of n in the formula is such that the compound has an average molecular weight of at least 1372, or at least about 10 mols of ethylene oxide for each mol of glycerol ricinoleate. The ethylene oxide units added to the glycerol ricinoleate molecule may be as high as 40 or more.

The increase of effective sensitivity of photographic silver halide emulsions with polyoxyethoxylated glycerol ricinoleates can be obtained in a number of ways. They may be added to an undercoating, to a middle coating, to an overcoating or to a surface coating prior to the coating operation. If desired, they may be added dur-ing the actual preparation of the emulsion either before or after washing of the emulsion.

The speed or sensitivity increasing agents of our invention may be used in various types of photographic emulsions, e.g., non-sensitized emulsions, orthochromatic, panchromatic, and X-ray emulsions. If used with sensitizing dyes, they may be added to the emulsion before or after the dyes are added. Various silver salts may be used as a sensitive element, such as silver bromide, silver iodide, silver chloride or mixed silver halides. The 60 polyoxyethoxylated glycerol ricinoleates may be used in emulsions intended for color photography, e.g., emul-sions containing color-forming components. The dispersing agent in the photographic emulsion may be gelatin or other colloids such as collodion, albumen, cellulose 65 derivatives, polyvinylalcohol or synthetic resins. The emulsion containing our novel sensitizer may be coated on any conventional base such as paper, glass, cellulose ester such as cellulose acetate, cellulose ethers and others.

The following specific examples are given of the man-70ner of using the novel sensitizer of our invention. It is to be understood, however, that these examples are given by way of illustration and not by way of limitation.

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#### 3 Example I

A silver halide emulsion in gelatin containing 4% silver iodide and 96% silver bromide was prepared in a conventional manner and brought up to its maximum light sensitivity. It was then readied for coating on film base, that is, melted at 40° C. and the necessary coating finals were added such as sensitizing dyes, stabilizers and hardeners. A 10% aqueous solution of an ethoxylated glycerol ricinoleate containing 12 to 13 mols of ethylene oxide per mol of glycerol ricinoleate was prepared and 1010 cc. of this solution were added to a sample of the above described emulsion containing about 0.4 mol of silver halide. A sample of the same emulsion but not containing the speed increasing additive served as a control. The so prepared emulsion samples were coated 15 on a suitable cellulose ester base and dried. Samples of these film coatings were then exposed in a Type IIB Sensitometer, developed in a developer of the following composition:

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Metol	1.5
Sodium sulfite, anhydrous	45.0
Sodium bisulfite	1.0
Hydroquinone	3.0
Sodium carbonate, monohydrated	6.8
Potassium bromide	
Water to make 1.0 liter.	

The results obtained were as follows:

Quantity of Polyethoxy-		Fog	
lated Gly- cerol Ricino- leate, gram	Relative	After 12' Dev.	6 Days Oven Test and 4' Dev.
0 1	100 160	. 14 . 23	.08 .14

#### Example II

A silver halide emulsion in gelatin containing 4% silver iodide and 96% silver bromide was coated on film

base. After coating, an aqueous gelatin solution containing 20 grams of gelatin per liter and 1.2 grams of the polyethoxylated glycerol ricinoleate of Example I was coated thereon as an anti-abrasion layer. After drying, film samples were exposed and processed as described in Example I. The samples exhibited a relative speed of 175 with a fog of .16 as compared with a type coating of the same emulsion having an anti-abrasion layer similar to that described above, but lacking the speed increasing additive and having a speed of 100 and a fog of .12.

Our invention is not limited to the detailed description contained herein, but includes all modifications that fall within the scope of the appended claims.

We claim:

1. A photographic material comprising a light-sensitive organic colloid silver halide emulsion having in contact therewith a component in addition to the colloid, said component comprising a water-soluble polyoxyethoxy-20 lated glycerol ricinoleate having an average molecular

weight of at least 1372 to increase the sensitivity thereof. 2. A photographic material as recited in claim 1 wherein the polyoxyethoxylated glycerol ricinoleate contains from 12 to 13 mols of ethylene oxide per mol of glycerol

25 ricinoleate. 3. A light-sensitive organic colloid silver halide emulsion containing as a sensitizer therefor in addition to the colloid a water-soluble polyoxyethoxylated glycerol ricinoleate having an average molecular weight of at least 30 1372.

4. A photographic material comprising a base and a layer of a light-sensitive organic colloid silver halide emulsion on said base, said layer being overcoated with another layer comprising a water-soluble polyoxyethoxy-35 lated glycerol ricinoleate having an average molecular

weight of at least 1372.

### References Cited in the file of this patent UNITED STATES PATENTS

2,728,666	Carroll Dec. 27, 1955
2,735,790	Waitkus Feb. 21, 1956
2,691,004	Doyle Oct. 5, 1960