United States Patent Office 2,937,087 Patented May 17, 1960

2,937,087

SILVER HALIDE EMULSIONS

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No Drawing. Application September 30, 1957 Serial No. 686,869

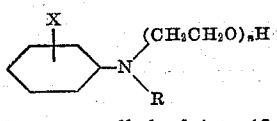
8 Claims. (Cl. 96—87)

This invention relates to radiation-sensitive silver halide emulsions of increased sensitivity. More particularly, it relates to such emulsions which contain as the sensitizing agent a condensation product of an N-alkylaniline with ethylene oxide which product contains at least three —CH_2CH_2O— groups. Still more particularly, it relates to photographic gelatino silver halide emulsions sensitized with such agents. The invention also relates to photographic elements bearing a layer of such emulsions.

It is known to increase the radiation response and contrast of silver halide emulsions by the addition of non-optical sensitizers. Useful such sensitizers are the polyalkylene glycols and their derivatives which are described in U.S. patents to Blake, Nos. 2,400,532, 2,423,549, and 2,441,389. However, these compounds tend to cause slight fog in emulsions to which they are added, particularly when photographic materials coated with said emulsions are stored for any length of time especially at high temperatures and humidities. Attempts to reduce this fog by combining this class of non-optical sensitizers with known antifogging agents have been tried but the use of such agents tends to reduce the beneficial speed increase contributed by the polyalkylene glycol sensitizer. This detrimental effect on speed is particularly noticeable when a photographic element is exposed to low intensity radiation.

An object of this invention is to provide silver halide emulsions of improved sensitivity. Another object is to provide such emulsions which have enhanced radiation response, particularly to low intensity radiation. Yet another object is to provide such emulsions which have good contrast. A further object is to provide such emulsions by means of the use of economical and effective non-optical sensitizers. A still further object is to provide such emulsions by a simple and dependable procedure. Still other objects will be apparent from the following description of the invention.

It has been discovered that the above objects can be attained and photographic silver halide emulsions of enhanced low-intensity response and contrast provided, in accordance with the invention, by incorporating with a radiation-sensitive water-permeable colloid silver halide emulsion sensitizing amounts of at least one condensation product of an unsubstituted N-monoalkylaniline, with or without an alkyl substituent in the aromatic nucleus, with ethylene oxide and containing at least three, or an average of at least three, oxyethylene groups. These condensation products can be represented by the general formula:



where X is hydrogen or alkyl of 1 to 18 carbon atoms, R is a normal or branched-chain alkyl radical of 1 to 18 carbon atoms and n is a positive integer of 3 to 25 or more. Thus, X is methyl, ethyl, propyl, butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or octadecyl.

The condensation product, or mixture of condensation products, wherein n represents the average number of such groups present, are incorporated with the emulsion or dispersion of silver halide in a water-permeable macromolecular organic colloid in an amount from about 0.05 to about 1.1 grams per mol of silver halide.

The product resulting from the above reaction has a composition represented by the above structure. Hence, when the ethylene oxide is used in an amount sufficient to introduce a certain weight of ethylene oxide, the resulting product has a composition wherein n represents an average value in the above structure.

The condensation products can be prepared in accordance with the exemplary procedure given below from aniline, a primary, secondary, tertiary or branched-chain alkyl bromide of 1 to 18 carbon atoms, e.g., methyl, ethyl, propyl, butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or octadecyl bromide and ethylene oxide. A mixture of two or more condensation products with different N-alkylanilines can be used if desired.

EXEMPLARY PROCEDURE

Two molar parts of alkyl bromide, e.g., n-dodecylbromide, were treated with 1500 parts of aniline and the mixture was allowed to stand overnight. A deposit of crystalline aniline hydrobromide was removed by filtration and the filtrate was heated to 120–130° C. for 3 to 4 hours to carry the reaction to completion (the aniline hydrobromide, removed by filtration above, was washed with acetone, the acetone evaporated, and the residue added to the main batch before the 3–4 hours heating period). The material was then washed 2 or 3 times in a separatory funnel with approximately 500 ml. portions of 20% sodium hydroxide solution to remove all hydrogen bromide.

The organic layer was distilled at atmospheric pressure through a short column to remove the excess aniline. The distillation was carried out until the pot temperature reached 290° C. The pot residue was transferred to a vacuum still and distilled to purify the N-alkylaniline formed. The distillation was carried out at a pressure of about 50 microns to yield 80–95% of the theoretical quantity of the N-alkylaniline.

One molar part of the purified N-alkylaniline and 2 ml. of boron trifluoride/diethyl ether complex were placed in a flask which was flushed with nitrogen gas to remove all oxygen. Ethylene oxide gas was then bubbled through the liquid at such a rate that good agitation was produced. The temperature of the mixture rose rapidly to about 100° C. and then gradually returned to room temperature. The contents of the flask were then heated to 140–150° C. while a gentle stream of nitrogen was passed through the flask to remove volatile substances, and after being cooled the product was transferred to a high vacuum still. This product was distilled at a pressure of about 50 microns to give a yield of 85–90% of the theoretical amount of the 2-(N-alkylanilino)ethanol.

One molar part of the purified 2-(N-alkylanilino)-ethanol was placed in an appropriate vessel, one-half part of freshly cut sodium was added, the vessel was flushed with a stream of nitrogen gas and the contents were heated to 140–150° C. in a stream of nitrogen until all of the sodium had dissolved. Ethylene oxide was then introduced until the weight gain indicated the absorption of the desired quantity of ethylene oxide. The product of this reaction, depending upon the alkyl halide used in the preparation of the alkylaniline, and also depending on the amount of ethylene oxide allowed to

condense with the 2-(N-alkylanilino)ethanol, is the desired product of the above general formula.

The invention is not limited to any particular type of light-sensitive silver halide as it is useful with silver chloride, silver bromide, silver iodobromide, silver chlorobromide, silver iodide, etc., emulsions and mixed emulsions of these types. It is particularly efficacious in silver iodobromide emulsions containing about 2 mole percent iodide and the rest bromide. These emulsions may be sensitized by means of the agents or adjuvants of the above structural formula and other sensitizers. Thus, noble metal sensitizers, for instance gold compounds, e.g., chlorauric acid and auric trichloride, may be present in association with sulfur sensitizers, e.g., sodium sulfite, thiosinamine, allylthiourea, sodium thiosulfate, allyl thiocarbamate, alkali metal thiocyanates and sodium sulfide, these sensitizers to be used in amounts up to 0.005% based on the weight of the silver halide. Moreover, the silver halide emulsions may contain one or more optical sensitizing agents, e.g., cyanine, carbocyanine, merocyanine, pseudocyanine, cyazine etc., dyes.

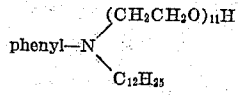
While gelatin is the preferred binding agent for the silver halide grains, other water-permeable amphoteric protein protective colloids, e.g., albumin and casein, can be used. Also, agar-agar, alginic acid and the alginates, polyglucuronic acid, polyvinyl alcohol, polyvinyl acetals including those containing color-forming nuclei, and other natural or synthetic water-permeable colloids useful in making photographic emulsions can be used as the original colloid during the precipitation, or in the final emulsion as bulking agents.

The adjuvants of the above structural formula preferably are added to the silver halide emulsion after it has been brought to its maximum sensitivity and the conventional adjuvants are added just prior to coating onto a suitable support to form a photographic element. They can, of course, be added at an earlier stage, that is, at the time of second digestion.

The invention will now be further illustrated by but is not intended to be limited to the following examples wherein the silver halide weight ratio, unless otherwise indicated, is 1.6 mole percent iodide and the remainder bromide. In these examples the emulsions were prepared and coated in the essential absence of actinic radiation, as is customary in the photographic art.

Example I

A gelatino-silver iodobromide emulsion containing 1.6 mole percent iodide was prepared and digested with an organic sulphur sensitizing compound and gold chloride. The emulsion was divided into two parts, one of which was used as a control. To the other part there was added as a final addition before coating 0.33 g. per mole of silver halide of a condensation product of N-dodecylaniline with ethylene oxide predominating in a compound having the formula:



The resulting emulsion was coated on a cellulose acetate film support and exposed to X-rays in the presence of an intensifying screen at two different intensity levels. The exposure of greater intensity is designated as No. 2 and that of lower intensity as No. 1. The exposed elements were developed for five minutes in a developer of the following composition:

	Grams
N-methyl p-aminophenol hydrosulfate	3
Sodium sulfite (anhydrous)	50
Hydroquinone	9
Potassium carbonate (anhydrous)	50
Potassium bromide	4.5
Water to make 1.0 liter.	

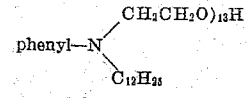
and fixed, washed and dried in a conventional manner.

The coatings were tested fresh, after room aging for one month and after one week at 120° F. and 65% relative humidity. The results of tests for speed, gamma and fog are given below. Speed is given in terms of a reciprocal of exposure at a density of 0.7.

	Fog	No. 2 Exposure		No. 1 Exposure	
		Speed	Gamma	Speed	Gamma
Fresh:					
Control	0.26	800	2.59	430	2.30
Compound	0.34	960	3.52	460	2.71
One Month Room Aging:					
Control	0.29	780	2.36	420	2.06
Compound	0.35	960	2.63	430	2.32
One Week 120° F., 65% R.H.:					
Control	0.36	720	2.06	460	2.06
Compound	0.42	980	2.38	560	2.13

Example II

A silver iodobromide emulsion was made and tested as in Example I except that 0.31 g. per mole of silver halide of a condensation product predominating in a compound having the following formula:



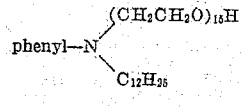
was added to the emulsion.

The results of the tests are as follows:

	Fog	No. 2 Exposure		No. 1 Exposure	
		Speed	Gamma	Speed	Gamma
Fresh:					
Control	0.26	800	2.59	430	2.30
Compound	0.27	930	3.54	460	2.70
One Month Room Aging:					
Control	0.29	780	2.36	420	2.06
Compound	0.24	920	2.66	450	2.34
One Week 120° F., 65% R.H.:					
Control	0.36	720	2.06	460	2.06
Compound	0.44	950	2.39	540	2.20

Example III

A silver iodobromide emulsion was made and tested as in Example I except that 0.30 gram per mole of silver halide of a condensation product predominating in a compound having the formula:



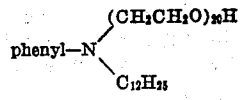
was added to the emulsion as a final addition. The results of the tests are as follows:

	Fog	No. 2 Exposure		No. 1 Exposure	
		Speed	Gamma	Speed	Gamma
Fresh:					
Control	0.26	800	2.59	430	2.30
Compound	0.24	980	3.56	490	2.77
One Week 120° F., 65% R.H.:					
Control	0.36	720	2.06	460	2.06
Compound	0.42	950	2.36	540	2.06

Example IV

A silver iodobromide emulsion was made and tested as described in Example I except that 0.30 g. per mole

of silver halide of a condensation product predominating in a compound having the formula:

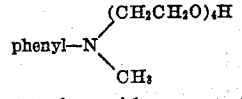


was added to the emulsion as a final addition. The results of the tests are as follows:

	Fog	No. 2 Exposure		No. 1 Exposure	
		Speed	Gamma	Speed	Gamma
Fresh:					
Control	0.36	800	2.59	430	2.30
Compound	0.28	950	3.52	430	2.43
One Month Room Aging:					
Control	0.29	780	2.36	420	2.06
Compound	0.49	940	2.33	510	2.00
One Week 120° F., 65% R.H.:					
Control	0.36	720	2.06	460	2.06
Compound	0.32	940	3.14	450	2.41

Example V

A silver iodobromide emulsion of a fine grain cine negative type was made containing about 6.8 mole percent iodide. The emulsion was digested with an organic sulfur compound and gold chloride. The emulsion was also optically sensitized with conventional carbocyanine dyes. To a portion of this emulsion there was added a final addition of 0.75 gram per mole of silver halide of a condensation product predominating in a compound having the formula:



This emulsion together with a control not containing the above compound were coated onto separate cellulose acetate film supports. They were exposed in an Eastman negative IB sensitometer and developed for 7 minutes at 68° F. in a developer of the following composition:

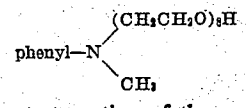
	Grams
N-methyl p-aminophenol hydrosulfate	0.80
Sodium sulfite (anhydrous)	90.00
Hydroquinone	1.0
Borax	3.0
Potassium bromide	0.10
Water to make 1.00 liter	

and fixed, washed and dried in a conventional manner. The coatings were tested fresh and after 10 days at 120° F. and 65% relative humidity. Results of tests for speed, gamma and fog are given below. Speed is expressed as a reciprocal of exposure at a density of 0.2.

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	112	0.61	0.07	80	0.05

Example VI

A silver iodobromide emulsion was made and tested as described in Example V except that 0.63 g. per mole of silver halide of condensation product predominating in a compound having the formula:

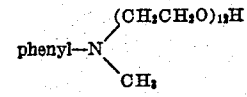


was added to the test portion of the emulsion as a final addition. The results of the test are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	112	0.68	0.07	70	0.06

Example VII

A silver iodobromide emulsion was made, coated, and tested in the manner described in Example V except that to the test portion of the emulsion there was added 0.61 g. per mole of silver halide of a condensation product predominating in a compound having the formula:

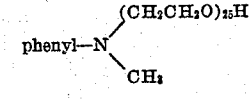


The results of the tests are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	112	0.72	0.07	80	0.05

Example VIII

A silver iodobromide emulsion was made, coated, and tested as described in Example V except that to the test portion there was added 0.60 g. per mole of silver halide of a condensation product predominating in a compound having the formula:

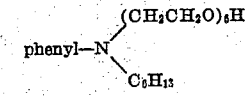


The results of the tests are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	163	0.72	0.10	130	0.08

Example IX

A silver iodobromide was made, coated and tested as described in Example V except that 0.71 g. per mole of silver halide of a condensation product predominating in a compound having the formula:



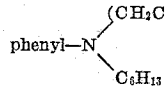
was added to the test portion of the emulsion. The results of the tests are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	112	0.66	0.07	70	0.07

Example X

A silver iodobromide emulsion was made, coated, and tested as described in Example V except to the test por-

tion of the emulsion there was added 0.69 g. per mole of silver halide of a compound having the formula:

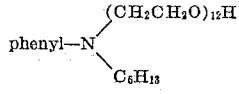


The results of the tests are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	120	0.71	0.08	75	0.08

Example XI

A silver iodobromide emulsion was made, coated, and tested as described in Example V except that to the test portion of the emulsion there was added 0.62 g. per mole of silver halide of a compound having the formula:

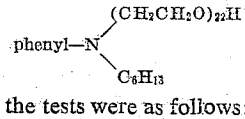


The results of the tests are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	140	0.72	0.07	70	0.07

Example XII

A silver iodobromide emulsion was made, coated, and tested in the manner described in Example V except that to the test portion of the emulsion there was added 0.60 g. per mole of silver halide of a compound having the formula:

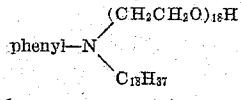


The results of the tests were as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	163	0.72	0.09	70	0.07

Example XIII

A silver iodobromide emulsion was made, coated, and tested in the manner described in Example V except that to the test portion of the emulsion there was added 0.67 g. per mole of silver halide of a condensation product predominating in a compound having the formula:

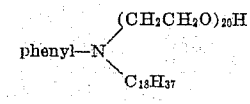


The results of the tests are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	140	0.68	0.06	85	0.07

Example XIV

A silver iodobromide emulsion was made, coated, and tested as described in Example V except that to the test portion of the emulsion there was added 0.65 g. per mole of silver halide of a compound having the formula:

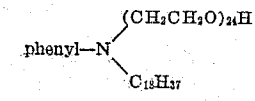


The results of the tests are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	140	0.72	0.08	85	0.07

Example XV

A silver iodobromide emulsion was made, coated, and tested in the manner described in Example V except that to the test portion of the emulsion there was added 0.62 g. per mole of silver halide of a condensation product of a compound having the formula:



The results of the tests are as follows:

	Fresh Tests			10 days 120° F., 65% R.H.	
	Speed	Gamma	Fog	Speed	Fog
Control	100	0.62	0.09	62	0.08
Anilino compound	140	0.74	0.08	90	0.11

In place of the alkyl groups shown on the nitrogen in the compounds of the examples, one may also have one of the following: ethyl, propyl, butyl, amyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl, tridecyl, pentadecyl, etc.

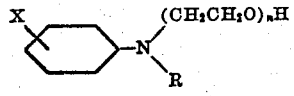
The invention is not limited to light-sensitive silver iodobromide emulsions but may be used with simple and mixed silver chloride, silver bromide and silver chlorobromide emulsions and mixtures of such emulsions. The aliphatic anilino polyoxyethylene compounds are usually added as one of the final additions just prior to coating but they may be added at any time after digestion. The emulsions may be coated on any suitable support to make the desired photographic element. Suitable supports include, in addition to the cellulose acetate set forth in the examples, other cellulose esters such as cellulose triacetate, cellulose acetate butyrate, cellulose nitrate, cellulose propionate; super polymers, e.g., nylon, polyethylene terephthalate, polyvinyl chloride, poly(vinyl chloride co vinyl acetate) and vinylidene chloride copolymers with vinyl acetate, acrylonitrile, etc.; metal sheets, e.g., aluminum and zinc; and paper including resin-coated and baryta-coated paper; as well as glass plates. The supports, of course, may have various sublayers to improve adherence to water-permeable organic colloids.

An advantage of the invention is that by the addition of a single compound there is obtained a high degree of non-optical sensitization without adversely affecting stability. A further advantage is that novel adjuvants are relatively inexpensive and are readily available or can be easily prepared.

What is claimed is:

1. A photographic silver halide dispersion in a gelatin binding agent, said dispersion containing in an amount

from about 0.05 to about 1.1 grams per mole of silver halide at least one compound of the formula



where X is a member taken from the class consisting of hydrogen and alkyl of 1 to 18 carbon atoms, R is an alkyl radical of 1 to 18 carbon atoms and *n* is a positive integer of at least 3.

2. A dispersion as defined in claim 1 wherein X is hydrogen, and *n* is 3 to 25.

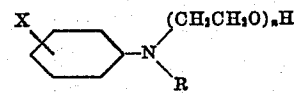
3. A dispersion as defined in claim 1 wherein said silver halide is silver iodobromide containing about two mole percent iodide and the rest bromide.

4. A dispersion as defined in claim 1 which contains an organic sulfur sensitizing agent.

5. A dispersion as defined in claim 1 which contains an organic sulfur sensitizing agent and a noble metal sensitizing agent.

6. A dispersion as defined in claim 1 wherein said silver halide is silver iodobromide.

7. A photographic element comprising a sheet support bearing a layer of a photographic silver halide dispersion in a gelatin binding agent, said dispersion containing in an amount from about 0.05 to about 1.1 grams per mole of silver halide at least one compound of the formula



where X is a member taken from the class consisting of hydrogen and alkyl of 1 to 18 carbon atoms, R is an alkyl radical of 1 to 18 carbon atoms and *n* is a positive integer of at least 3.

8. An element as defined in claim 7 wherein said support is a hydrophobic film.

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