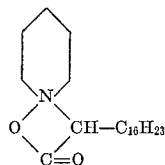


2

10 Claims 10

In accordance with the present invention it has been found that the new class of cation active compounds which may be obtained by substituting for a hydrogen atom of the  $\text{CH}_2$  group or for the  $\text{CH}_2$  group itself, in the above-identified betaine formula, a hydrocarbon group or derivative containing at least six and preferably from ten to eighteen carbon atoms are particularly useful in photographic compositions. It is also contemplated that the aforementioned higher hydrocarbon group may be substituted for one or more of the methyl groups, rather than for the  $\text{CH}_2$  group. Furthermore in place of one or more of the methyl groups, shown in said formula, other substituents, as for instance, other alkyl groups or aralkyl, aryl or cycloaliphatic groups may be substituted. In the same manner, the nitrogen nucleus may form an integral part of a heterocyclic ring, such as a pyridine or piperidine ring. This carbonyl group, may moreover, be substituted on some other substituent of the compound rather than upon the substituent which contains, or is, a long chain hydrocarbon group. Compounds of the essential betaine structure in which the nitrogen atom is separated from the carbonyl group by a single carbon atom are herein denoted as  $\alpha$ -betaines. Those in which the separations are by two carbon atoms as  $\beta$ -betaines etc.

The following specific compounds having a betaine formulation are useful and are representative of a large class of useful compounds: C-(n-hexadecyl)  $\alpha$ -betaine, N-(n-dodecyl)  $\alpha$ -betaine, N-(n-octadecyl)  $\alpha$ -betaine, N-(n-decyl)  $\alpha$ -betaine, N-(9,10-octadecenyl)  $\alpha$ -betaine, C-(n-hexadecyl) pyridinium  $\alpha$ -betaine of the formula



N-(n-tetradecyl)  $\alpha$ -betaine, N-(2-ethylhexyl)  $\alpha$ -betaine, N-(n-octadecyl)  $\beta$ -betaine.

Mixtures of any two or more of the betaine and other compounds referred to above can be used in making the silver halide emulsions by the herein described processes.

The process of this invention is conveniently carried out by mixing a dilute aqueous solution of at least one water-soluble inorganic halide, e.g., potassium bromide, potassium iodide, and ammonium chloride or mixtures of two or more such salts with an  $\alpha$ -betaine or  $\beta$ -betaine having at least one aliphatic hydrocarbon radical containing from 10 to 18 carbon atoms with a dilute aqueous solution of a water-soluble silver salt, e.g., silver nitrate, silver sulfate, silver sulfamate, silver citrate, silver acetate or a mixture of any of such silver salts. After the two solutions are mixed together, the mixture is allowed to ripen at ordinary or moderately elevated temperatures, e.g., 25° C. to 50° C. until the silver halide grains have achieved the desired size and distribution. In general, ripening times from 15 minutes to one hour will be found sufficient to provide grains having the proper size and distribution. In general, longer ripening times tend to produce the larger crystals which are especially useful in high-speed photographic emulsion layers. After ripening, the silver halide grains can be washed free of soluble salts resulting from the reaction forming the silver halides by lowering the pH to about 2.0 with a strong mineral acid, e.g., nitric, sulfuric and hydrochloric acids. Other acids such as acetic acid may be used as long as they are photographically inert and have a dissociation constant at least as great as acetic in order to avoid the use of excessive amounts of acid. The lowering of the pH coagulates the betaine compound which settles out of solution carrying the silver halide grains with it while the soluble salts remain in solution and can be removed by decanting the supernatant liquid.

The remaining silver halide grains produced by the process can be used to prepare photographic emulsions by dispersing them in an aqueous solution of a protective colloid binder, e.g. gelatin, albumin, casein, synthetic binders, e.g. polyvinyl alcohol, water-soluble polyvinyl acetals, water-soluble polyamides, water-soluble cellulose derivatives and the like. The pH of any binder solution should be adjusted to between 6.3 and 6.5 to allow the betaine carrying the silver halides to be completely re-dispersed. After redispersion, the emulsion may be chilled and stored or may be digested immediately in the presence of gold and sulfur sensitizers or other adjuvants conventionally used to obtain optimum photographic properties.

Photographic emulsions prepared from the silver halide crystals obtained by the process of this invention have good photographic quality and are suitable for coating on conventional photographic supports, e.g., transparent film base, paper, glass plates, etc.

The invention will now be further illustrated but is not intended to be limited by the following examples which are carried in the absence of actinic radiations.

#### EXAMPLE I

A solution made from 500 ml. of 6% aqueous solu-

tion of C-cetyl betaine, 625 ml. of 3 molar  $\text{NH}_4\text{Cl}$  and 20 ml. of an aqueous  $\text{HCl}$  solution containing 0.0002 g. of rhodium chloride was added, with agitation and at a temperature of 113° F., to 2500 ml. of an aqueous solution containing 1.5 moles of silver nitrate and to the resulting mixture there was added 150 ml. of a 3 molar aqueous solution of potassium bromide. The resulting dispersion was held at 120° F. for 15 minutes and then cooled. To the mixture there was then added 600 ml. of 0.06 M sulfuric acid to adjust the pH to about 2.0. After allowing the resulting coagulant to settle 15 minutes the supernatant liquid was decanted. The coagulant was then washed with 2500 ml. of water containing 23 ml. of 3 molar sodium chloride and 25 ml. of 0.06 M sulfuric acid. There is then added with stirring to the washed coagulant, a solution containing 200 ml. of water, 25 grams of photographically inert gelatin and 14 ml. of 0.06 M sodium hydroxide. The pH of the dispersion was adjusted to 6.3–6.5 with 0.06 M sodium hydroxide. The resulting redispersion was made up to 950 ml. with water and added with stirring to an aqueous solution containing 2250 ml. of water and 140 grams of photographically inert gelatin. The resulting mixture was digested for 45 minutes at about 120° F. during which there were added a gold sensitizer, a sulfur sensitizer and an orthochromatic dye sensitizer together with antifogging agent, and the usual final adjuvants including coating aids and hardening agents, all of which is conventional in the art. The final emulsion was coated on a transparent photographic quality film support and dried by the usual photographic manufacturing techniques to give a coating weight of 70 milligrams per square decimeter based on the silver nitrate.

The resulting photographic film together with an all gelatin control conventional film were exposed on an intensity scale (IB type) sensitometer with a tungsten lamp operating at 2877° K. using a 78AA Wratten color correction filter and a  $\sqrt{2}$  step wedge with 126 meter candle seconds at the exposure plane.

The exposed films were developed for two minutes at 68° F. in a lithographic developer having the following composition:

	Grams
Hydroquinone	22.5
Sodium sulfite (anhyd.)	30.0
Sodium bisulfite	2.2
Boric acid	7.5
Potassium bromide	1.6
Paraformaldehyde	7.5
Water to make 1.0 liter.	

immersed in an acetic acid short stop for a few seconds, fixed in a conventional acid hardening fixer and washed for 10 minutes and dried. The following sensitometric results were obtained:

Characteristic	C-cetyl betaine make	Conventional emulsion
100/E speed at 2.00 density	20.0	18.0
Total scale value	8.5	5.0
$D_{\text{max}}$	4.0*	4.0*
Effective contrast	4.8	9.3
Fog	.015	.000

#### EXAMPLE II

A solution made up of 500 ml. of a 6% aqueous solution of C-cetyl betaine and 625 ml. of a 3 molar ammonium chloride solution was added with agitation and at a temperature of 113° F. to 2500 ml. of an aqueous solution containing 1.5 moles of silver nitrate and to the resulting mixture there was added 150 ml. of a 3 molar solution of potassium bromide. The resulting dispersion was held at 120° F. for 15 minutes and then cooled. To the mixture there was then added 600 ml. of 0.6 M sulfuric acid to adjust the pH to about 2.0. After allowing the resulting coagulant to settle for 15 minutes, the supernatant liquid was decanted. The

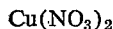
5

coagulant was then washed with 2500 ml. of water containing 23 ml. of 3 molar sodium chloride and 25 ml. of 0.06 molar sulfuric acid. There is then added with stirring to the washed coagulant, a solution containing 200 ml. of water, 50 ml. of ethyl alcohol and 25 grams of polyvinyl alcohol 99-100 hydrolyzed (High Viscosity Grade 72-60 "Elvanol" manufactured and sold by E. I. du Pont de Nemours & Co.). The pH was raised to  $6.3 \pm 1$  with aqueous sodium hydroxide to complete redispersion of the coagulant. The resulting mixture was added to a solution containing 1330 ml. of water, 260 ml. of ethyl alcohol and 133 grams of the above described polyvinyl alcohol. This addition was made at a temperature of  $126^\circ \text{F}$ . The resulting emulsion was digested for 30 minutes at  $126^\circ \text{F}$ . during which there was added a gold sensitizer, a sulfur sensitizer and an orthochromatic sensitizing dye together with an anti-fogging agent and the usual final adjuvants including surfactant coating aids and hardening agents. The emulsion was coated on a photographic grade paper support at a coating weight of 70 mg./dm.<sup>2</sup> calculated as silver nitrate.

The resulting film was exposed and processed in the manner described in Example I with sensitometric results which were comparable to those obtained in that example.

### EXAMPLE III

A contact type emulsion was made in the manner that is disclosed in Example I except that 0.003 g. of rhodium chloride and 40 ml. of 1.5 molar copper nitrate



was added to the aqueous ammonium chloride solution of C-cetyl betaine before the addition to the silver nitrate solution. All other operations including coating and drying were the same as in Example I. The film was exposed as described in that Example I to give the following sensitometric data:

Characteristic	C-cetyl betaine	Conventional film
100/E at 2.00.....	0.0395	0.0655
Total scale value.....	6.9	7.8
$D_{\text{max}}$ .....	4.0 <sup>+</sup>	4.0 <sup>+</sup>
Gamma.....	6.0	5.2
Fog.....	0.00	0.00

The process of the invention has been illustrated in the examples with specific mention of certain betaine compounds as silver halide dispersing agents. However, the process is not limited to these specific agents but can be carried out with those betaines mentioned in the foregoing part of the specification. The compounds are easily made by adding a suitable acid such as chloroacetic acid to a tertiary amine containing at least one aliphatic radical containing at least 12 carbon atoms and neutralizing the mixture with a suitable alkali.

While the examples illustrate the invention with certain silver halide systems, it is by no means so limited. It may be used with other silver halide emulsions which are useful in the graphic arts, radiological fields and other uses. For example good quality silver chlorobromide, bromochloride and iodobromide emulsion useful in the graphic arts, data recording, engineering reproduction and radiological film can be made.

The invention is a new process of preparing dispersing silver halides for photographic purposes. The process of the invention is equally applicable to preparing either gelatino-silver halide emulsions or photographic silver halide emulsions having synthetic colloid binders as indicated above. It is particularly useful in preparing gelatin emulsions because it simplifies the emulsion preparation. This is particularly true where the emulsions are washed by the method of coagulating the gelatin. No complexing or other reaction agent except acids are necessary to coagulate the emulsions to remove the soluble salts resulting from the precipitation of silver halides.

6

A further advantage of one aspect of this invention is that the conventional extensive washing procedures are not required. Thus, as the betaine compound does not absorb as much of the soluble salt by-products as does gelatin, washing is not necessary. Instead, simple decantation removes enough of the soluble salts to prevent restraint of sensitivity.

I claim:

1. A process for the preparation of light-sensitive silver halide which comprises precipitating, in the absence of actinic radiation and a water-permeable colloid, at least one silver halide in an aqueous solution in the presence of at least one inner salt of a pentavalent nitrogen compound of the general formula:



wherein X represents an atom selected from the group consisting of Cl and Br;

R<sub>1</sub> is an aliphatic hydrocarbon radical of 12-18 carbon atoms;

R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each aliphatic hydrocarbon radicals of less than 8 carbon atoms and wherein at least one of the radicals R contains a carboxylic acid group.

2. A process for the preparation of light-sensitive silver halide which comprises:

(a) precipitating in the absence of actinic radiation at least one silver halide by admixing at least one water-soluble silver salt with at least one water-soluble halide in an aqueous solution in the absence of a water-permeable colloid and in the presence of at least one inner salt of a pentavalent nitrogen compound of the general formula



wherein X represents an atom selected from the group consisting of Cl and Br;

R<sub>1</sub> is an aliphatic hydrocarbon radical of 12-18 carbon atoms;

R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each aliphatic hydrocarbon radicals of less than 8 carbon atoms and wherein at least one of the radicals R contains a carboxylic acid group; and

(b) separating the precipitated silver salt from the aqueous solution.

3. A process for the preparation of light-sensitive silver halide dispersions which comprises:

(a) precipitating at least one silver halide by admixing at least one water-soluble silver salt with at least one water-soluble halide in an aqueous solution in the absence of a water-permeable colloid and in the presence of at least one inner salt of a pentavalent nitrogen compound of the general formula



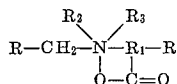
wherein X represents an atom selected from the group consisting of Cl and Br;

R<sub>1</sub> is an aliphatic hydrocarbon radical of 12-18 carbon atoms;

R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each aliphatic hydrocarbon radicals of less than 8 carbon atoms and wherein at least one of the radicals R contains a carboxylic acid group;

7

- (b) separating the precipitated silver salt from the aqueous solution; and  
 (c) dispersing the precipitated silver halide in an aqueous solution of a water-permeable colloid; said steps being carried out in the absence of actinic radiation.
- 5 4. A process according to claim 3 wherein the colloid is gelatin.
- 10 5. A process for the preparation of light-sensitive silver halide which comprises precipitating in the absence of actinic radiation and a water-permeable colloid at least one silver halide in an aqueous solution in the presence of at least one pentavalent nitrogen compound of the general formula:

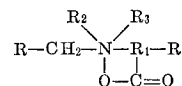


wherein one of the radicals R represents an alkyl radical of 9-17 carbon atoms and the other radical R is a hydrogen atom, R<sub>1</sub> is a methylene radical and R<sub>2</sub> and R<sub>3</sub> are alkyl radicals of less than 8 carbon atoms.

6. A process according to claim 5 wherein said nitrogen compound is C-cetylbetaine.
- 25 7. A process for the preparation of light-sensitive silver halide which comprises
- (a) precipitating in the absence of actinic radiation and a water-permeable colloid at least one silver halide by admixing at least one water-soluble silver salt with at least one water-soluble halide in the

8

presence of at least one pentavalent nitrogen compound of the general formula:



wherein one of the radicals R represents an alkyl radical of 9-17 carbon atoms and the other radical R is a hydrogen atom, R<sub>1</sub> is a methylene radical and R<sub>2</sub> and R<sub>3</sub> are alkyl radicals of less than 8 carbon atoms, and

- (b) separating the precipitated silver salt from the aqueous solution.
8. A process according to claim 7 wherein said nitrogen compound is C-cetylbetaine.
- 15 9. A process according to claim 7 including the additional step,
- (c) dispersing the precipitated silver halide in an aqueous solution of a water-permeable colloid; said steps being carried out in the absence of actinic radiation.
10. A process according to claim 9 where the colloid of step (c) is gelatin.

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