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SILVER SALTS OF PYRIDINE CARBOXYLIC ACIDS AND PHOTOGRAPHIC EMULSIONS CONTAINING THE SAME

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ABSTRACT OF THE DISCLOSURE

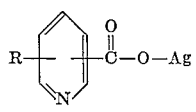
This invention relates to silver salts of pyridine carboxylic acids and processes for preparing the same. In one aspect emulsions of the new silver salts exhibit photographic properties.

This invention relates to light sensitive compositions. In one of its aspects this invention relates to certain novel light sensitive organic silver compounds. In another of its aspects, this invention relates to photographic systems and methods that employ organic silver compounds.

The silver halides known in the prio art are generally the basis of photographic systems which have been found to be practical for photographic purposes. Certain organic acid silver salts have also been mentioned as being light sensitive and capable of development. However, the known organic acid silver salts have never achieved significant commercial recognition as their sensitiviy to light is two to three times lower than that of the slowest silver halides generally used in present photographic elements.

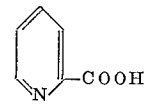
It is accordingly an object of the present invention to provide a novel organic silver salt having sensitivity to radiation similar to that achieved in silver chloride emulsions. Another object is to provide a novel photographic system comprising the novel organic silver salts. Another object is to provide novel means for obtaining photographic reproductions. Another object is to provide a photographic element containing a novel organic silver salt. Still another object is to provide an organic silver salt system with a photographic speed similar to that of conventional contact silver halide papers. Other objects and advantages will appear from the following description and claims.

According to the present invention photographic systems employ as a light-sensitive element a silver salt of a pyridine carboxylic acid having the following formula:

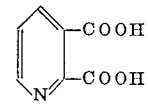


wherein R represents substituents in one or more positions on the ring and can be hydrogen atoms, alkyl groups, alkoxy groups, carboxylic acid groups, carboxyalkylene groups, groups containing a carboxylic acid silver salt radical, and the like. Preferably the R substituents are hydrogen atoms, carboxy groups, groups containing carboxylic acid silver salt radicals and the like. In certain preferred embodiments substantially all of the carboxy radicals on said compound form carboxylic acid silver salt radicals.

Typical preferred compounds which form silver salts useful in photographic emulsions include picolinic acid having the formula:



quinolinic acid or pyridine-2,3-dicarboxylic acid having the following formula:



and like compounds.

An important feature of this invention is the discovery of an organic silver salt which has a photographic speed comparable with conventional silver halide contact papers. Moreover, the ripening step often used with silver halide emulsions is not necessary with the new compounds of this invention to produce high sensitivity photographic elements.

Various methods may be used to make the silver salt of pyridine carboxylic acids. For example, one method for the synthesis of a radiation sensitive silver picolinate is to react a pyridine carboxylic acid, such as picolinic acid, with a soluble silver salt such as silver nitrate. The reaction proceeds in aqueous solution; preferably the temperature is maintained at from about 30° C. to about 40° C. Generally any water-soluble silver salt can be used in the reaction such as silver sulfate, silver acetate, silver nitrate, silver perchlorate, and the like, or it can be a silver salt such as p-toluene sulfonate silver salt, and other suitable organo-silver complexes. Organic silver salts can also be chosen that will release to the solution, upon reaction with the pyridine carboxylic acid, an organic ion that is useful in a photographic emulsion, such as an acid, dye, hardener, etc. For example, silver p-toluenesulfonate, uopn reaction with picolinic acid will release sulfonic acid which contributes acid for a photographic emulsion. However, in the present invention the silver salt is preferably silver nitrate or ammoniacal silver nitrate. The use of ammoniacal silver nitrate is preferred as it allows one to reduce the gelatin concentration in the preparation of an emulsion and increases the speed of the resultant emulsion.

In a preferred embodiment of this invention a hydrophilic colloid such as pigskin gelatin is used as the film forming binder. However, various colloids can be used in combination with the gelatin as vehicels or binding agents in the photographic emulsions ad elements employed in the practice of this invention. Among such materials are the natural and/or synethetic binding materials generally employed for this purpose including, for example, colloidal albumin, water soluble vinyl polymers as exemplified by mono and polysaccharides, cellulose derivatives, proteins, water soluble polyacrylamides, polyvinyl pyrrolidone and the like. In addition to the hydrophilic colloids, the vehicle or binding agents can contain dispersed polymerized vinyl compounds, particularly those which increase the dimensional stability of photographic materials. Suitable synthetic polymers of this type

include the water insoluble acrylic interpolymers such as those containing units of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The various layers of the photographic elements of this invention can be hardened with any suitable hardener, including for example, aldehyde hardeners, aziridine hardeners, hardeners which are derivatives of dioxane, oxypolysaccharides such as oxy-starch, oxy plant gums and the like.

The photographic layers described herein can be coated on a wide variety of supports. Typical flexible supports include those generally employed for photographic elements such as cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film and related films or resinous materials as well as, thin glass films, paper, and the like. Supports, such as paper, which are partially acetylated or coated with baryta or an α-olefin polymer, particularly a polymer of an α-olefin containing 2–10 carbon atoms, as exemplified by polyethylene, polypropylene, ethylene butene copolymers and the like also give good results.

The photographic emulsions and elements of this invention can also contain additional addenda, particularly those known to be beneficial in photographic materials of this nature. For example, they can contain stabilizers or antifoggants such as organic azoles, azaindenes, mercaptans, metal salts such as cadmium, lead, mercury, gold or other noble metal salts, spectral sensitizers such as the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, hemicyanines, speed increasing materials, such as polyalkylene glycols, onium salts and thio ethers, plasticizers, coating aids such as anionic, non-ionic and amphoteric surface active compounds and the like.

Inorganic and organic compounds may be added to the emulsion to adjust the pH value. Acids such as nitric, sulfuric, p-toluene sulfonic and the like may be used for this purpose. The optimum photographic properties for a pigskin gelatin emulsion are obtained at a pH of about 4. Depending upon the particular binding agents and addendum incorporated in the emulsion, the pH can be approximately adjusted to obtain the desired properties.

The organic silver salts can be coated on a film support by any suitable emulsion coating method to produce a light sensitive layer on the support.

The development and fixing of emulsions containing the silver salt of pyridine carboxylic acids can be generally carried out by methods applicable to silver halide emulsions. A developer which has been found especially satisfactory is sodium hydroxide-hydroquinone-elon developer.

For example, when the development is carried out in a rapid process machine (for 1 to 2 seconds), the following developing solution may be used:

Water—1 liter
Ethanol—100 ml.
Elon—15 g.
Na_2SO_3, anhydrous—50 g.
Hydroquinone—15 g.
NaOH—15 g.
Potassium bromide—2 g.
pH=11

Other developing solutions need longer development times. For example, the developing time is about 15 seconds with the following developer.

Water—1 liter
Elon—2 g.
Na_2SO_3 anhydrous—35 g.
Hydroquinone—5 g.
Na_2CO_3—25 g.
Potassium bromide—1 g.
pH=10

All those developing solutions may be used between 23° C. and 32° C. and, in general, the development rate increases with the pH of the developer.

The fixing solution can generally be any fixing solution used for silver halide emulsions.

The invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that the examples are included merely for purposes of illustration and are not intended to limit the scope of the invention unless otherwise indicated.

EXAMPLE 1

Eight grams of pigskin gelatin are swollen in 100 ml. of water. Twenty-five ml. of 0.6 N picolinic acid are added to this solution. Twenty-five ml. of 0.2 N silver nitrate are then added dropwise while stirring the mixture. The pH is maintained at about 4. The precipitation temperature is maintained at about 40° C. The emulsion is coated on a paper support at a coverage rate of 6 to 7 mg. of silver per dm.^{2} and is dried.

The coated paper is exposed for 2 seconds to a tungsten 100 w. lamp placed at 20 cm. from an original. The exposed coating is then developed for 5 seconds in a developer obtained by mixing 500 ml. of composition A with 3 ml. of composition B:

Composition A

	G.
Elon	2.25
Na_2SO_3 anhydrous	7.0
Hydroquinone	9.0
Na_2CO_3	25.0

Water, to make 1 liter.

Composition B

	G.
KBr	1.0
Benzothiazole	0.20

Water, to make 1 liter.

and fixed with a hypo solution. The D_{max} of the developed print is about 1.3 and the contrast is about 0.90. After exposing the images to a 250 w. xenon lamp for 4 hours no increase in fog is noticeable whereas the fog increase in a control silver chloride reflex copying type paper processed under the same conditions is 0.15.

The photographic speed of the silver picolinate coated paper is approximately that of a conventional contact speed silver chloride paper.

EXAMPLE 2

Twelve grams of pigskin gelatin are disposed in 230 ml. of water. Twenty ml. of 0.6 N picolinic acid are then added. Fifty ml. of ammoniacal silver nitrate are then added to the mixture over a period of about 20 minutes. The pH is maintained at about 4. Precipitation conditions are maintained for this mixture at about 40° C.

The emulsion is coated on a paper support at a coverage rate of 6 to 7 mg. of silver per dm.^{2} and dried. The coated paper is then dried, exposed, developed and fixed as in Example 1. The coated paper has a photographic speed suitable for contact printing, approximately that of a silver chloride emulsion. The finished print has a neutral-tone silver image of good gradation. The D_{max} of developed image was about 1.4 and the contrast was about 0.95.

EXAMPLE 3

Precipitation conditions of Example 2 are repeated, but picolinic acid is replaced by an equivalent amount of quinolinic acid.

The emulsion is coated on a paper support as mentioned in Example 2. The coated paper is then dried and exposed for 2 seconds to a tungsten 300 w. lamp placed at 30 cm. from an original. The exposed paper is then developed and fixed as in Example 1. The finished print has a neutral-tone silver image of good gradation. The

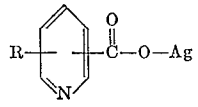
D_{max} of the deevloped image is about 1.05 (above fog) and the contrast was about 0.83.

Similar images are obtained with other silver salts of pyridine carboxylic acids such as isonicotinic acid, pyridine-2, 6-dicarboxylic acid, pyridine-2,5-dicarboxylic acid, and the like.

The invention has been described with reference to preferred embodiments thereof, but it will be understood that variations and modifications of the invention can be made within the scope of the following claims.

We claim:

1. A photographic emulsion comprising a compound having the formula:



wherein R represents substituents in one or more positions on the ring of hydrogen atoms, alkyl groups, alkoxy groups, carboxylic acid groups, carboxyalkylene groups, or groups containing a carboxylic acid silver salt radical.

2. An emulsion according to claim 1 wherein said emulsion comprises silver picolinate.

3. An emulsion according to claim 1 wherein said emulsion comprises pigskin gelatin.

4. An emulsion according to claim 1 wherein substantially all R substituents on said compound are hydrogen atoms or groups containing a carboxylic acid silver salt radical.

5. A photographic element comprising a support and at least one layer thereon comprising an emulsion according to claim 1.

6. A photographic element according to claim 5 wherein said emulsion comprises silver picolinate.

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