

UNITED STATES PATENT OFFICE

2,553,500

PRODUCTION OF PHOTOGRAPHS IN
BLUE-BLACK TONES AND COMPOSITIONS
THEREOFHarold C. Harsh, Binghamton, N. Y., assignor to
General Aniline & Film Corporation, New
York, N. Y., a corporation of DelawareNo Drawing. Application August 1, 1946,
Serial No. 687,713

8 Claims. (Cl. 95-88)

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This invention relates to a photographic process for producing blue-black tones in silver images, to photographic elements, and to photographic developer and treating solutions containing blue-black toning agents.

Various organic compounds for the production of photographs from silver-halide emulsions in blue-black tones have been suggested from time to time. Thus, for example, benzotriazole, nitrobenzimidazole, and the like, have been employed for this purpose. These compounds, however, have the disadvantage of gradually decomposing in the developer as a result of which they considerably retard development. Moreover, these compounds are very sensitive to oxidizing and reducing agents usually employed in photographic developers so that the blue-black toning effect of the developer very rapidly diminishes and after a time ceases altogether.

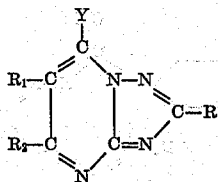
In accordance with the present invention, blue-black shades or tones are obtained while avoiding all of the aforementioned shortcomings and disadvantages of the prior proposals.

An object of the present invention is to provide a process for the production of blue-black tones in silver-halide emulsions.

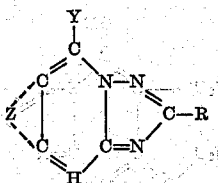
A further object is to provide a new class of blue-black toning agents which are added to a photographic developer.

Other objects and advantages of the present invention will be readily apparent from the following description.

I have found that the foregoing objects are accomplished by the use of hydroxy- and amino-1,3,4-triazaindolizines characterized by the following general formulae:



and



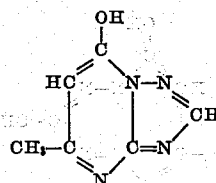
wherein R and R₁ are hydrogen, lower alkyl, e. g., methyl, ethyl, propyl, isopropyl, butyl, amyl, and

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the like, 5- or 6-membered alicyclic ring structure, e. g., cyclopentyl, cyclohexyl, and the like, aryl, e. g., phenyl, naphthyl, diphenyl, etc., or a 5- or 6-membered heterocyclic radical containing not more than two hetero atoms, e. g., pyridyl, furyl, pyrrol, pyrazolyl, and the like, R₂ is amino, hydroxy, carbalkoxy, e. g., carbomethoxy, carbethoxy, carbpropoxy, and the like, or an alkyl, aryl, alicyclic, or heterocyclic radical of the same value as R, Y is an amino or hydroxy group, and Z represents the atoms necessary to complete either a five-membered or six-membered alicyclic or heterocyclic ring structure of the same value as given for R.

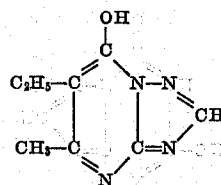
Typical compounds corresponding to the foregoing general formula which are included in this invention, are as follows:

(1)



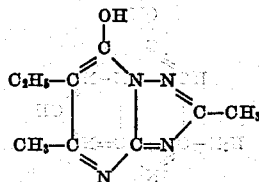
7-hydroxy-5-methyl-1,3,4-triazaindolizine

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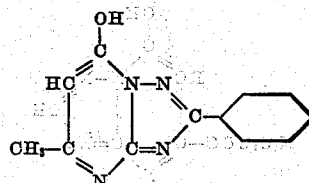
7-hydroxy-6-ethyl-5-methyl-1,3,4-triazaindolizine

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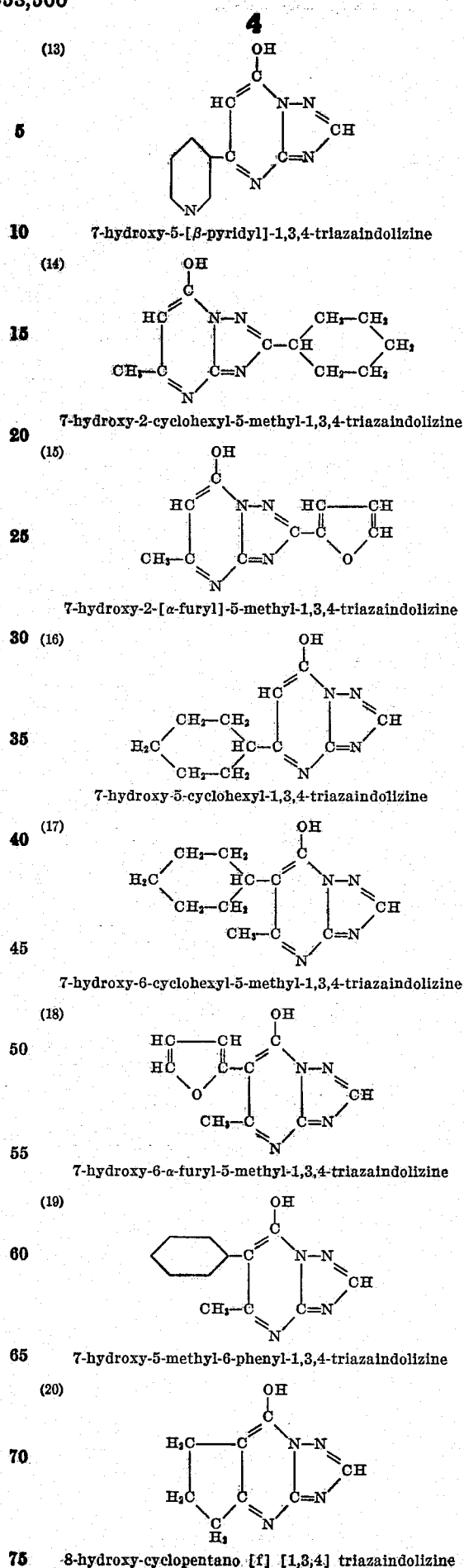
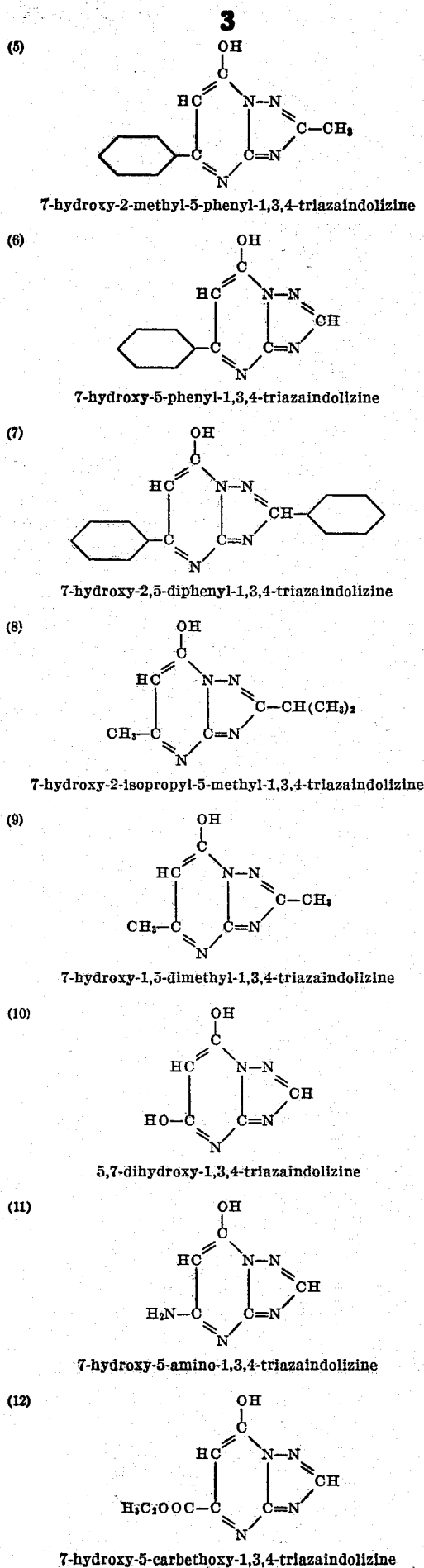


7-hydroxy-6-ethyl-2,5-dimethyl-1,3,4-triazaindolizine

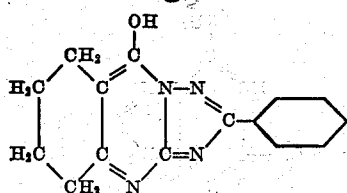
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7-hydroxy-5-methyl-2-phenyl-1,3,4-triazaindolizine

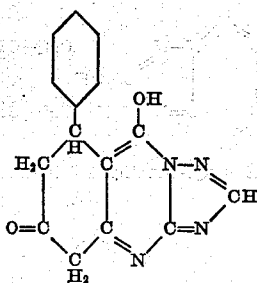


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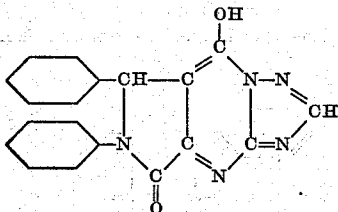
9-hydroxy-2-phenyl-cyclohexano [f] [1,3,4] triazaindolizine

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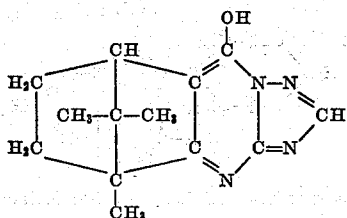
9-hydroxy-6-oxy-8-phenyl-cyclohexano [f] [1,3,4] triazaindolizine

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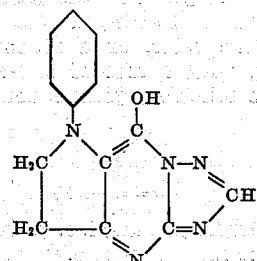
8-hydroxy-5-oxy-6,7-diphenyl-pyrrolidino [3,4-f] [1,3,4] triazaindolizine

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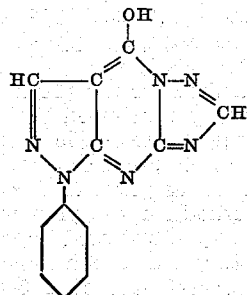
9-hydroxy-5-methyl-5,8-dimethylmethano-cyclohexano [f] [1,3,4] triazaindolizine

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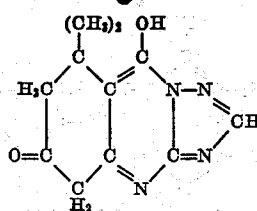
8-hydroxy-7-phenyl-pyrrolidino [4,5-f] [1,3,4] triazaindolizine

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8-hydroxy-5-phenyl-Δ²-pyrazolidino [5,4-f] [1,3,4] triazaindolizine

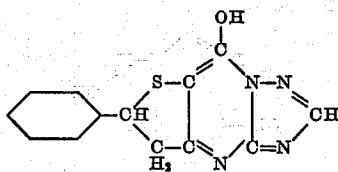
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9-hydroxy-8,8-dimethyl-6-oxy-cyclohexano [f] [1,3,4] triazaindolizine

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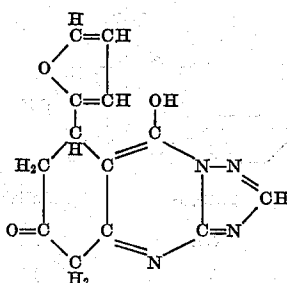


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8-hydroxy-6-phenyl-thiolano [4,5-f] [1,3,4] triazaindolizine

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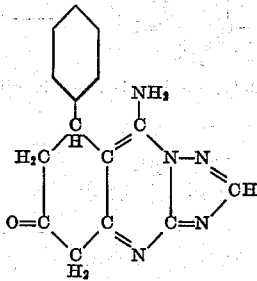
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9-hydroxy-8-α-furyl-6-oxy-cyclohexano [f] [1,3,4] triazaindolizine

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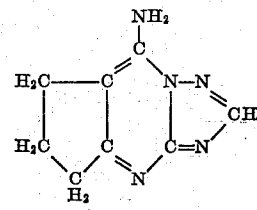


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9-amino-6-oxy-8-phenyl-cyclohexano [f] [1,3,4] triazaindolizine

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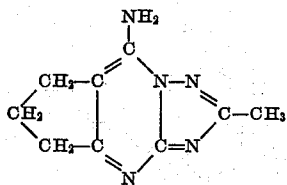


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8-amino-cyclopentano [f] [1,3,4] triazaindolizine

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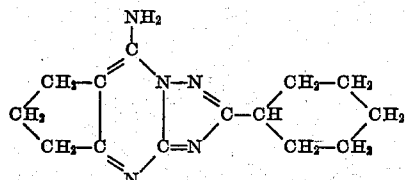
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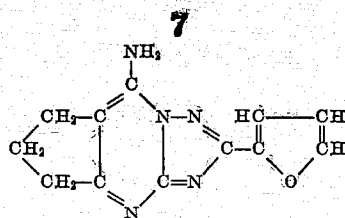
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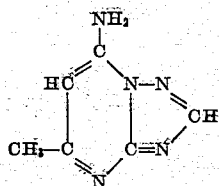


8-amino-2-cyclohexano-cyclopentano [f] [1,3,4] triazaindolizine

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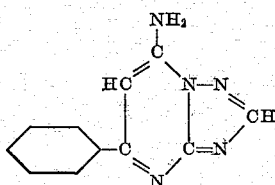
8-amino-2- α -furyl-cyclopentano [f] [1,3,4] triazaindolizine

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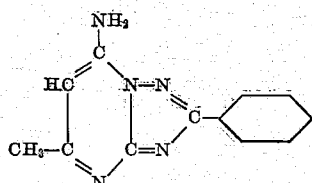
7-amino-5-methyl-1,3,4-triazaindolizine

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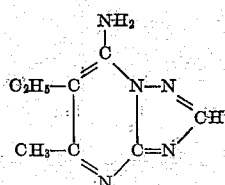
7-amino-5-phenyl-1,3,4-triazaindolizine

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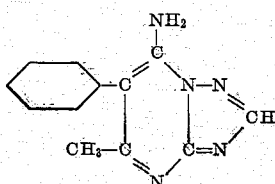
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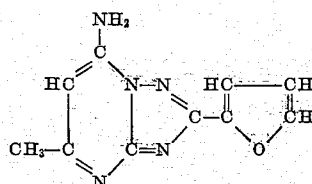
7-amino-6-ethyl-5-methyl-1,3,4-triazaindolizine

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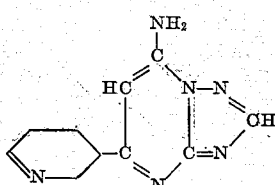


7-amino-5-methyl-6-phenyl-1,3,4-triazaindolizine

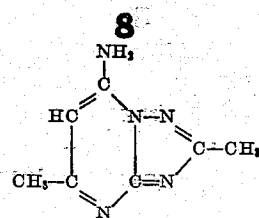
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7-amino-2- α -furyl-5-methyl-1,3,4-triazaindolizine

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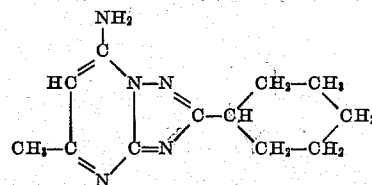
7-amino-5- β -pyridyl-1,3,4-triazaindolizine

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7-amino-2,5-dimethyl-1,3,4-triazaindolizine

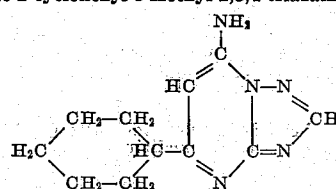
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7-amino-2-cyclohexyl-5-methyl-1,3,4-triazaindolizine

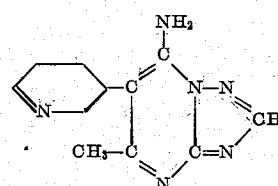
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7-amino-5-cyclohexyl-1,3,4-triazaindolizine

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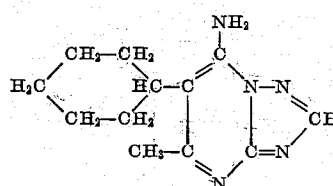


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7-amino-6- β -pyridyl-1,3,4-triazaindolizine

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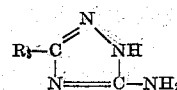
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7-amino-5-methyl-6-cyclohexyl-1,3,4-triazaindolizine

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The method for the preparation of the hydroxy-1,3,4-triazaindolizines illustrated by compounds 1 to 19 is given in the literature. The method consists of heating 1 mol of a β -keto ester, a malonic ester, or a mononitrile of a malonic ester, with 1 mol of a 3-amino-1,2,4-triazole of the following general formula:

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wherein R_3 is hydrogen, alkyl, e. g., methyl, ethyl, propyl, and the like, or aryl, e. g., phenyl, naphthyl, diphenyl, and the like. The reaction is described more fully for compound 2 in *Berichte* 42, page 4643, and for compounds 3, 5, and 9 in *Berichte* 43, pages 378-380. The same conditions herein described were applied in the preparation of compounds 1, 4 to 8, and 12 to 19, inclusive. The method for the preparation of the product of the type illustrated by compound 10 consists of heating 1 mol of a malonic ester with 1 mol of a 3-amino-1,2,4-triazole, under the same reaction conditions as given in the above references. The method for the preparation of the product of the type illustrated by compound 11 consists of heating 1 mol of a mononitrile of a malonic ester with 1 mol of a 3-amino-1,2,4-triazole.

75 The method for the preparation of the hy-

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droxy-1,3,4-triazaindolizines, illustrated by compounds 20 to 46, inclusive, by condensing a β -keto ester with a 3-amino-1,2,4-triazole is given in the aforementioned references. By substituting a cyclic β -keto ester or nitrile, a β -imino nitrile, or a β -keto nitrile for the β -keto ester and employing the same reaction conditions described in these references, the amino- and hydroxy-1,3,4-triazaindolizines utilized in accordance with this invention are readily prepared.

The blue-black toning agents of the present invention are preferably used in developing solutions in which they diffuse to the exposed silver halide grains and produce a blue-black toning effect during the course of development.

The degree of blue-black tones obtained upon development varies somewhat with the silver-halide ratio of the emulsion used in coating the film, plate, or paper support containing the toning agents. Optimum results, i. e., most pleasant blue-black tones, are obtained with silver chloride emulsions where the ratio of silver bromide to silver chloride by weight is less than 1 to 40. With silver-halide emulsions, which are especially prepared to give colder tones, the photographic material, i. e., film, plate, or paper, containing the toning agents, blue-black toning effects are still obtained where the ratio of silver bromide to silver chloride is 1 to 2. These silver-halide emulsions may also carry silver iodide up to one part of silver iodide by weight to 20 parts of the silver bromide and silver chloride combined.

The concentration of the particular toning agent in developing solutions may vary from 20 mg. to 100 mg. per liter. The most desirable concentration, however, can be readily determined by conducting a few simple experiments.

The invention will be further illustrated, but is not intended to be limited, by the following examples.

Example I

A metol-hydroquinone developer of the following composition was prepared:

Hot water (125° F. or 52° C.)	cc.	750
p-Monomethyl-amine-m-phenol sulfate	grams	3.5
Sodium sulfite (anhydrous)	do.	45
Hydroquinone	do.	11.5
Sodium carbonate (monohydrate)	do.	78
Potassium bromide	do.	1.2
Water to make	liter	1

To this developer solution, 60 mgs. of 7-amino-5-methyl-1,3,4-triazaindolizine were added. Upon development of an exposed gelatino silver-halide emulsion, containing silver bromide and silver chloride in the ratio of 1 to 40, respectively, blue-black tones were produced in the silver image.

Example II

Example 1. was repeated with the exception that an equivalent quantity of 7-hydroxy-5-[β -pyridyl]-1,3,4-triazaindolizine was substituted for 7-amino-5-methyl-1,3,4-triazaindolizine.

It will be apparent that the amounts of the foregoing toning agents may vary with the different types of photographic and developing compositions. The optimum quantities, however, required for a particular composition can be readily determined by a few simple tests. After exposure, developing, fixing, and drying, the image obtained is of a blue-black color instead of

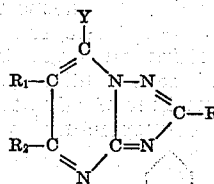
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the brownish-black or black obtained with an untreated element.

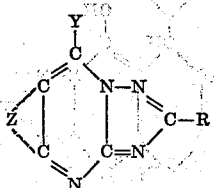
While I have, in this specification, specifically described several embodiments which my invention may assume in practice, it will be further understood that the same are shown for purposes of illustration only and that the invention may be further modified and embodied in various other forms without departing from the spirit or scope of the appended claims.

I claim:

1. The process for producing developed silver pictures in blue-black tones which comprises developing an exposed light-sensitive silver-halide emulsion layer, with an aqueous solution of an alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent, said solution containing from 20 to 100 mgs. per liter of said developer a 1,3,4-triazaindolizine selected from the class consisting of those corresponding to the general formulae:

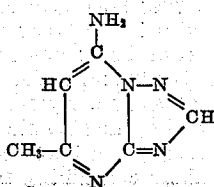


and



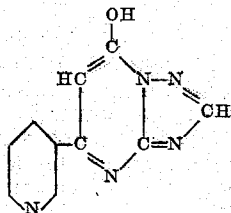
wherein R and R₁ are members selected from the class consisting of hydrogen, lower alkyl, aryl, an alicyclic ring structure of from 5 to 6 carbon atoms, and a heterocyclic group of from 5 to 6 members containing not more than two hetero atoms. R₂ is a member selected from the class consisting of amino, hydroxy, alkyl, carbalkoxy, aryl, and alicyclic ring structure of from 5 to 6 carbon atoms, and a heterocyclic group of from 5 to 6 members containing not more than two hetero atoms, Y is a member selected from the class consisting of amino and hydroxy, and Z represents the atoms necessary to complete a member selected from the class consisting of a 5-membered and 6-membered alicyclic ring structure and a 5-membered and 6-membered heterocyclic ring structure containing not more than two hetero atoms.

2. The process for producing developed silver pictures in blue-black tones which comprises developing an exposed light-sensitive silver halide emulsion layer with an aqueous solution of an alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent, said solution containing from 20 to 100 mgs. per liter of said developer a 1,3,4-triazaindolizine corresponding to the formula:

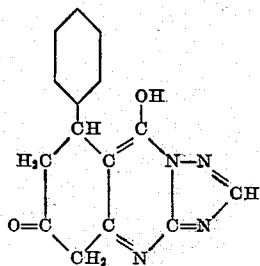


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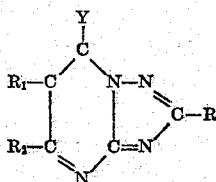
3. The process for producing developed silver pictures in blue-black tones which comprises developing an exposed light-sensitive silver-halide emulsion layer with an aqueous solution of an alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent, said solution containing from 20 to 100 mgs. per liter of said developer a 1,3,4-triazaindolizine corresponding to the formula:



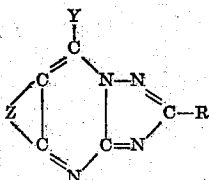
4. The process for producing developed silver pictures in blue-black tones which comprises developing an exposed light-sensitive silver-halide emulsion layer with an aqueous solution of an alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent, said solution containing from 20 to 100 mgs. per liter of said developer a 1,3,4-triazaindolizine corresponding to the formula:



5. A photographic developer for development of exposed light-sensitive silver-halide emulsions consisting of an aqueous solution of an alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent, said solution containing from 20 to 100 mgs. per liter of said developer a 1,3,4-triazaindolizine selected from the class consisting of those corresponding to the general formulae:



and

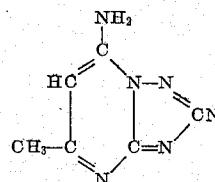


wherein R and R₁ are members selected from the class consisting of hydrogen, lower alkyl, aryl, an alicyclic ring structure of from 5 to 6 carbon atoms, and a heterocyclic group of from 5 to 6 members containing not more than two hetero atoms, R₂ is a member selected from the class consisting of amino, hydroxy, alkyl, carbalkoxy, aryl, and alicyclic ring structure of from 5 to 6 carbon atoms, and a heterocyclic group of from 5 to 6 members containing not more than

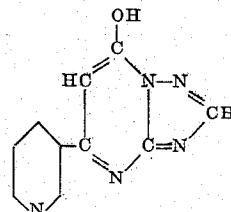
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two hetero atoms, Y is a member selected from the class consisting of amino and hydroxy, and Z represents the atoms necessary to complete a member selected from the class consisting of a 5-membered and 6-membered alicyclic ring structure and a 5-membered and 6-membered heterocyclic ring structure containing not more than two hetero atoms.

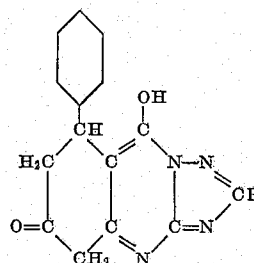
6. A photographic developer for development of exposed light-sensitive silver-halide emulsions consisting of an aqueous solution of an alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent, said solution containing from 20 to 100 mgs. per liter of said developer a 1,3,4-triazaindolizine of the formula:



7. A photographic developer for development of exposed light-sensitive silver-halide emulsions consisting of an aqueous solution of an alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent, said solution containing from 20 to 100 mgs. per liter of said developer a 1,3,4-triazaindolizine of the formula:



8. A photographic developer for development of exposed light-sensitive silver-halide emulsions consisting of an aqueous solution of an alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent, said solution containing from 20 to 100 mgs. per liter of said developer a 1,3,4-triazaindolizine of the formula:



HAROLD C. HARSH.

REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
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2,158,184	Heckman et al.	May 16, 1939
2,390,707	Heimbach	Dec. 11, 1945
2,432,419	Heimbach	Dec. 9, 1947
2,444,605	Heimbach	July 6, 1948
2,444,606	Heimbach	July 6, 1948
2,444,607	Heimbach	July 6, 1948