

United States Patent [19]
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[11] **3,910,792**
[45] **Oct. 7, 1975**

[54] **GUANAZYL AND GUANAZILIUM SALT
COMPOUNDS AS ANTIFOG AGENTS FOR
SILVER HALIDE EMULSIONS**

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[22] Filed: **Apr. 29, 1974**

[21] Appl. No.: **465,186**

[30] **Foreign Application Priority Data**

May 10, 1973 Italy 49895/73

[52] U.S. Cl. **96/76 R; 96/109**

[51] Int. Cl.² **G03C 1/34**

[58] Field of Search 96/109, 107, 66.5, 76 R

[56]

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3,071,465 1/1963 Dersch et al. 96/109

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[57]

ABSTRACT

Guanazyl and guanazylium salt compounds are effective antifog agents for silver halide photographic emulsions when reactively associated therewith. Such compounds can be incorporated in the photographic element in reactive association with the silver halide emulsion or in a processing bath prior to or during the development of emulsion layers.

23 Claims, No Drawings

GUANAZYL AND GUANAZILIUM SALT COMPOUNDS AS ANTIFOG AGENTS FOR SILVER HALIDE EMULSIONS

This invention relates to guanazyl and guanazylum salt compounds as antifog agents for silver halide photographic emulsions.

As it is known, the problem of fog, that is silver reduced in unexposed areas upon development which forms spurious images, is one of the most important problems to be solved in the photographic chemistry. This problem has become more critical since high temperature baths are used containing aldehydes as hardening agents.

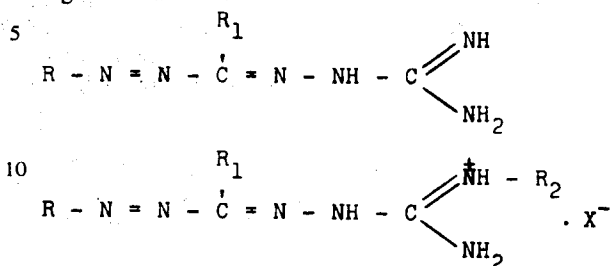
We have now found that guanazyl and guanazylum salt compounds are very effective agents both used in a photographic element reactively associated with the silver emulsion and in a processing bath adapted for use prior to or during development of emulsion layers. They can also be used in combination with high temperature processing baths containing or not aldehydes as hardening agents. Guanazylum salt compounds have proven to be more effective than guanazyl compounds when directly introduced into a bath to be used prior to or during development of silver halide emulsions.

Accordingly, the invention relates in one aspect to a silver halide emulsion having contacted therewith a guanazyl and/or a guanazylum salt compound. In another aspect the invention relates to a silver photographic element having a silver emulsion layer and a guanazyl and/or a guanazylum salt compound in reactive association therewith (e.g. in a layer adjacent the emulsion layer). The invention in a further aspect relates to a method for inhibiting fog in a silver halide photographic emulsion which comprises contacting said emulsion with a guanazyl and/or guanazylum salt compound. The invention further relates to an improved method for processing an exposed silver halide element, which includes treating said element with a series of photographic treatment solutions including a development solution, the improvement comprising contacting said element during said processing with a guanazyl and/or guanazylum salt compound, preferably a guanazylum salt compound, said compound being contained in said development solution and/or in a predevelopment treatment solution. In another aspect the invention relates to a processing solution

adapted for use prior to or during development of a silver photographic element, containing or not an aldehyde as hardener, containing a fog inhibiting amount of a guanazyl and/or guanazylum salt compound, preferably a guanazylum salt compound.

Guanazyl and guanazylum salt compounds as a class have proven to be useful as fog inhibiting agents for silver halide emulsions when reactively associated therewith. The substituents attached to their molecule or the nature of the anion, in the case of guanazylum salt compounds, do not substantially vary the capacity of the compounds to inhibit fog.

The compounds useful according to the present invention are preferably those represented by the following formulas:



wherein

R is an aryl group;

R₁ is an aryl group or a heterocyclic group;

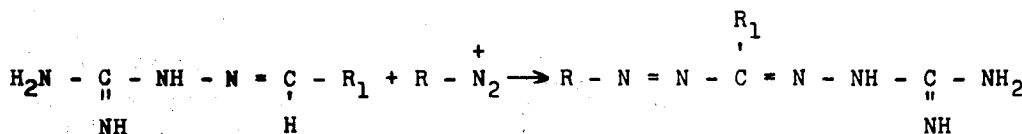
R₂ is an alkyl group or hydrogen; and

X is an anion such as, for example, halogen (e.g. chloride, iodide) and picrate.

An aryl group as used in the practice of this invention is a preferably phenyl or naphthyl group with substituents, if any, selected from at least one of halogen, alkyl, alkoxy, perfluoroalkyl, haloalkyl, nitro and acyl groups. These substituent groups each have no more than six carbon atoms when attached to the phenyl group and no more than two carbon atoms when attached to the naphthyl group. The total number of carbon atoms in R and R₁ is preferably no more than 12, and for R₂, preferably no more than four carbon atoms. The molecular weight of R and R₁ is preferably no more than 300 and more preferably no more than 200. For R₂, the preferred molecular weight is no more than 60.

The heterocyclic group used in the practice of this invention as group R₁ preferably has a total molecular weight of no more than 300 and more preferably at most 200. The most preferred group is pyridine. Substituents in the heterocyclic group are preferably limited to those same substituent groups preferred for the aryl group of R and R₁ as phenyl. Preferred heterocyclic groups are five and six membered rings, the skeletal structure of such rings consisting of carbon, nitrogen, oxygen, sulfur, and selenium with groups consisting of carbon and nitrogen, with at most one oxygen or sulfur atom most preferred.

The guanazyls of the present invention were prepared by known processings (Chem. Review 55, 401 (1955), which are based on the reaction of an aryl-diazonium salt with a guanylhydrazone, according to the scheme:



Such a reaction is strongly influenced by the pH-value and conditioned by the use of a suitable solvent. The guanazylum salts thereof were prepared by reacting the guanazyl compounds with a salifying agent (e.g. pyric acid and methylchloride or iodide as known to the skilled in the art).

The conditions adopted in the preparation of specific compounds of the present invention are, however, shown with more details in the following examples.

EXAMPLE 1

1-3-diphenyl-guanazyl

9.3 g of aniline (0.1 moles) were diazotated in 30 ml of concentrated HCl (0.3 moles) and 30 ml of water at 0°–2°C with 7.5 g (0.11 moles) of sodium nitrite. A solution of guanyldiazone nitrate, 22.5 g (0.1 moles) in 250 ml of water added with 4 g of NaOH in 50 ml of water and 60 g of sodium acetate in 200 ml of water was prepared apart. The diazonium chloride solution was dropped into the guanyldiazone solution at –2°C. The pH-value of the reaction product was adjusted from 5–6 to 10 with sodium hydrate, thus obtaining the separation of a red dusty solid, which was then filtered, dried in the air and crystallized from ethyl acetate.

M.P.–199°C with decomposition.

Yield-22 g (85% of the theoretical yield).

EXAMPLE 2

1-(m-trifluoromethyl-phenyl)-3-phenyl guanazyl

32.2 g (0.2 moles) of m-trifluoromethylaniline in 60 ml of HCl and 260 ml of water are diazotated with 13.8 g of sodium nitrite (0.2 moles) at 0°–2°C. A solution of 45 g (0.2 moles) of guanazyl-hydrazone dissolved in 1 l of methanol was prepared apart. The aryldiazonium chloride solution was then dropped into the guanyldiazone solution at 0°C. 45 g of sodium acetate in 200 ml of water were then added thereto as a buffering solution and the pH-value adjusted to 8–8.5 with a 30% NaOH solution. A dark solid separated slowly. It was then collected by filtration, washed with water, dried and purified by crystallization.

M.P.–179°C with decomposition.

Yield-71 g (62% of the theoretical yield).

EXAMPLE 3

1-(p-chlorophenyl)-3-phenyl-guanazyl

25.5 g (0.2 moles) of p-chloro-aniline in 60 ml of HCl and 60 ml of H₂O were diazotated at 0°–5°C with 13.8 g (0.2 moles) of sodium nitrite. A solution consisting of 45 g (0.2 moles) of guanyldiazone benzaldehyde nitrate in 1 l of methanol was prepared apart. This solution was then cooled at 0°C and the aryldiazonium solution, prepared before, dropped therein maintaining the temperature at 0°C. 45 g of sodium acetate in 200 ml of water were then added thereto. The pH-value was adjusted from 6 to 8.5 with 30% NaOH. The solid was separated by suction, then washed with water, dried and crystallized from acetic ester.

M.P.–188°C with decomposition.

Yield-18 g (32% of the theoretical yield).

EXAMPLE 4

1-phenyl-3(p-tolyl)-guanazyl

18.6 g (0.2 moles) of aniline with 60 ml of HCl and 60 ml of H₂O were diazotated with 13.8 g (0.2 moles) of sodium nitrite and the diazo-solution was dropped at 0°C into a solution of 47.8 g of p-tolylaldehyde-guanyldiazone nitrate (0.2 moles) in 2,000 ml of methanol. 45 g of sodium acetate in 200 ml of water were added to the reaction product and the pH-value of the solution, thus obtained, adjusted to 8–8.5 with 30% sodium hydrate. A powdery product separated. It was then washed, dried and finally purified by crystallization from ethanol.

M.P.–174°C with decomposition.

Yield-7.8 g (14% of the theoretical yield).

EXAMPLE 5

1-(p-tolyl)-3-phenyl-guanazyl

42.8 g (0.4 moles) of p-toluidine were diazotated and the diazo-solution dropped at 0°C into a solution of 90 g (0.4 moles) of benzaldehyde guanyldiazone nitrate in 2 l of methanol. A solution of 90 g of sodium acetate and then 30% NaOH, to adjust the pH to 8.5, were then added to the reaction product, thus obtained. A dark-red powdery product separated. It was then washed, dried and purified by crystallization from ethyl acetate.

M.P.–144°C with decomposition.

Yield-24.8 g (22% of the theoretical yield).

EXAMPLE 6

1-phenyl-3(o-chloro-phenyl)-guanazyl

18.6 g (0.2 moles) of aniline were diazotated and the diazo-solution, at 0°C, was added to 51.8 g (0.2 moles) of o-chlorobenzaldehyde guanyldiazone nitrate in 1 l of methanol plus 45 g of sodium acetate in 200 ml of water and 30% NaOH to adjust the pH to 11. When the diazo-addition approached to the end, an orange-red powdery product started to separate. The raw solid was purified by crystallization from nitromethane.

M.P.–209°C with decomposition.

Yield-32 g (53% of the theoretical yield).

EXAMPLE 7

1-phenyl-3-(p-nitro-phenyl)-guanazyl

4.5 g of the p-nitro-benzaldehyde-guanyldiazone base were dissolved in 400 ml of ethanol. The solution was cooled at –5°C and a solution of diazonium chloride, obtained by diazotating 2.02 g (0.022 moles) of aniline, dropped therein. The solution, thus obtained, was poured into 4 l of water and its pH-value adjusted to 12 with 30% NaOH. A solid separated. It was then purified by crystallization from nitromethane.

M.P.–195°C with decomposition.

Yield-2 g (30% of the theoretical yield).

EXAMPLE 8

1-(m-nitro-phenyl)-3-phenyl-guanazyl

12 g (0.074 moles) of guanyldiazone benzaldehyde, as a free base, were dissolved in 200 ml of ethanol and 75 ml of water, cooled at –10°C and added with a solution prepared by diazotating 10.5 g (0.076 moles) of m-nitro-aniline in 26.2 ml of HCl. The pH-value was adjusted to 8 with NaOH and an orange colored solid separated rapidly. This solid was then collected, dried and purified by crystallization from ethanol.

M.P.–190°C with decomposition.

Yield-12.4 g (54% of the theoretical yield).

EXAMPLE 9

1-3-diphenyl-guanazylum-chloride

16.2 g (0.1 moles) of guanyldiazone benzaldehyde were dissolved in 200 ml of ethanol and 100 ml of water and processed at –10°C with a solution obtained by diazotating 9.3 g (0.1 moles) of aniline in 30 ml of HCl. The pH-value of the reaction product was maintained at 5 and the solution concentrated to approximately one half. A brick-red solid separated. It was then purified by crystallization from chloroform.

M.P.–202°C with decomposition.

Yield-17.8 g (59% of the theoretical yield).

EXAMPLE 10

1-3-diphenyl-guanazylum iodide

15.1 g (0.05 moles) of 1,3-diphenylguanazyl chlorohydrate (example 9) were dissolved in 200 ml of ethanol and then added with 10 g of potassium iodide. The raw iodide separated upon concentration. The product was then purified by several recrystallizations.

M.P.-185°C with decomposition.

Yield-15 g (70% of the theoretical yield).

EXAMPLE 11

1-3-diphenyl-N-methyl-guanazylum-iodide

5.3 g (0.02 moles) of 1,3-diphenylguanazyl (example 1) in 60 ml of methanol were refluxed with 14.1 g of methyl iodide for 5 hours. The product thus obtained was then crystallized from nitromethane.

M.P.-186°C with decomposition.

Yield-4.05 g (50% of the theoretical yield).

EXAMPLE 12

1-(p-chlorophenyl)-3-phenyl-guanazylum-picrate

3 g (0.01 moles) of 1-(p-chloro)-3-phenylguanazyl (example 3) were dissolved in 60 ml of boiling ethanol and added first with 3 ml of hydrochloric acid and afterwards with an excess (0.05 moles) of picric acid in a saturated water solution, thus obtaining tiny red needles:

M.P.-208°C with decomposition.

Yield-3.4 g (65% of the theoretical yield).

EXAMPLE 13

1-phenyl-3-(o-chlorophenyl)-guanazylum-picrate

3 g (0.01 moles) of 1-phenyl-3-(o-chlorophenyl)-guanazyl (example 6) were processed as described in example 12. The product was crystallized from ethanol.

M.P.-203°C with decomposition.

Yield-4.15 g (78% of the theoretical yield).

EXAMPLE 14

1-(m-trifluoromethyl-phenyl)-3-phenyl-guanazylum-picrate

3.34 g (0.01 moles) of 1-(m-trifluoromethyl)-3-phenylguanazyl (example 2) were processed as described in example 12. The product was crystallized from ethanol.

M.P.-199°C with decomposition.

Yield-4.6 g (82% of the theoretical yield).

EXAMPLE 15

1-3-diphenyl-guanazylum-picrate

2.66 g (0.01 moles) of 1,3-diphenylguanazyl (example 1) were processed as described in example 12. The product was crystallized from ethanol.

M.P.-197°C with decomposition.

Yield-4.2 g (85% of the theoretical yield).

EXAMPLE 16

1-(p-chloro-phenyl)-3-phenyl-N-methyl-guanazylum-iodide

3 g (0.01 moles) of 1-(p-chloro-phenyl)-3-phenyl-guanazyl (example 3) in 50 ml of methanol were heated for 7 hours with 10 ml of methyl-iodide. The product was crystallized from ethanol.

M.P.-182°C with decomposition.

Yield-3.5 g (75% of the theoretical yield).

EXAMPLE 17

1-phenyl-3-(γ -pyridine) guanazylum chloride

8.15 g (0.05 moles) of γ -pyridinaldehydeguanyldrazone were dissolved in 20 ml of pyridine and 200 ml of ethanol and further added at -5°C with a solution obtained by diazotating 4.65 g (0.05 moles) of aniline in 15 ml of HCl. An orange-red solution having a pH value equal to 6-7 was obtained and an orange-colored crystalline product separated by standing. The product was crystallized from ethanol.

M.P.-222°C with decomposition.

Yield-5.1 g (34% of the theoretical yield).

EXAMPLE 18

A highly sensitive silver bromo-iodide emulsion, containing 98.2% bromide moles and 1.8% iodide moles, was physically ripened, washed, chemically sensitized and further divided into more parts. A part was kept like it was and the others added with compounds Nos. 1-8 of the present invention in the quantities specified in table 3. The said parts were separately coated on a cellulose triacetate base and covered with a gelatin protective layer. Samples of the material, thus obtained, were exposed fresh or incubated to the light of a tungsten lamp and developed for 3' at 20°C with a developer having the following composition:

Methol	22.- g
Hydroquinone	8.8 g
Sodium sulfite, anhydrous	72.- g
Potassium bromide	4.- g
Sodium carbonate, anhydrous	48.- g
Water to make	1 l

The same samples were fixed (with a normal thiosulphate fixing bath), washed and dried, then evaluated with a normal densitometer. The results are shown in table 1 (Acet., EtOH and DMF respectively indicate the solvent used to introduce the fog-inhibiting compound into the emulsion: Acet. means acetone, EtOH means ethylalcohol and DMF means dimethyl formamide).

TABLE 1

Compound	mM/MAGX	Solvent	Fresh		Aged 15 h. at 30% R.H. and 72°C	
			Relative Sensitivity	Fog	Relative Sensitivity	Fog
—	—	—	100	0.24	100	0.22
1	0.5	Acet.	77	0.10	85	0.10
2	0.5	EtOH	77	0.11	83	0.11
3	0.5	EtOH	63	0.07	78	0.07
4	0.1	DMF	20	0.05	58	0.07
5	0.1	DMF	73	0.13	80	0.11
6	0.1	DMF	103	0.11	94	0.14
7	0.1	DMF	96	0.18	104	0.19
8	0.1	DMF	86	0.12	88	0.11

EXAMPLE 19

8
a densitometer. The results thereof are shown in table 2.

TABLE 2

Compound	mM/MagX	Solvent	Fresh		Aged 15 h. at 30% R.H. and 72°C	
			Relative Sensitivity	Fog	Relative Sensitivity	Fog
—	—	—	100	0.45	100	0.41
1	0.5	Acet.	89	0.18	85	0.15
2	0.5	EtOH	88	0.19	88	0.15
3	0.5	EtOH	77	0.10	77	0.11
4	0.1	DMF	25	0.09	39	0.10
5	0.1	DMF	83	0.25	84	0.20
6	0.1	DMF	102	0.19	102	0.19
7	0.1	DMF	93	0.28	95	0.27
8	0.1	DMF	82	0.19	85	0.20

Samples of the material described in example 18 were exposed to the light of a tungsten lamp and developed with the following developer:

Methol	3 g
Sodium sulfide, anhydrous	50 g
Hydroquinone	9 g
Glutaraldehyde disulfite	13 g
Sodium carbonate, anhydrous	50 g
Potassium bromide	3 g
Water to make	1,000 ml.
Acetic acid to adjust the pH to	10.1

The temperature of the developing bath was 35°C and the development time 23 seconds. After development, the material was fixed in a bath including glutaraldehyde having the following composition:

20 A highly sensitive emulsion, having the same characteristics as that used in example 18, was divided into more parts.

25 A part was kept like it was without any further addition, the others were added with compounds Nos. 9–17 of the present invention in the quantity specified in table 3. The said parts were then separately coated on a cellulose triacetate base and covered with a gelatin protective layer. Samples of the material, thus obtained, were exposed to a tungsten lamp and processed as those of example 18. The samples, processed either fresh or after aging, were read at a densitometer. The results thereof are shown in table 3.

TABLE 3

Compound	mM/MagX	Solvent	Fresh		Aged 15 h. at 30% R.H. and 72°C	
			Relative Sensitivity	Fog	Relative Sensitivity	Fog
—	—	—	100	0.27	100	0.25
9	0.5	DMF	90	0.11	95	0.14
10	0.1	DMF	91	0.14	94	0.14
11	0.1	DMF	96	0.19	97	0.16
12	0.1	DMF	93	0.18	94	0.18
13	0.1	DMF	85	0.15	85	0.14
14	0.1	DMF	90	0.16	90	0.18
15	0.5	DMF	90	0.15	84	0.14
16	0.5	DMF	92	0.19	102	0.19
17	0.1	DMF	40	0.09	18	0.08

EXAMPLE 21

Sodium sulfite, anhydrous	50 g
Sodium thiosulfate pentahydrate	400 g
Glutaraldehyde disulfite	13 g
Water to make	1,000 ml.

and washed and dried for a total processing time of 90 seconds. The samples, thus obtained, were then read at

50 Samples of either fresh or aged materials of example 18 were exposed to the light of a tungsten lamp and developed for 23 seconds at 35°C with a developer, fixed and washed for a total processing time of 90 seconds as in example 19.

The samples, thus obtained, were then read at a densitometer. The results thereof are shown in table 4.

TABLE 4

Compound	mM/MagX	Solvent	Fresh		Aged 15 h. at 30% R.H. and 72°C	
			Relative Sensitivity	Fog	Relative Sensitivity	Fog
—	—	DMF	100	0.42	100	0.40
9	0.5	DMF	85	0.20	87	0.20
10	0.1	DMF	97	0.21	95	0.16
11	0.1	DMF	104	0.16	101	0.23
12	0.1	DMF	102	0.24	100	0.21
13	0.1	DMF	100	0.16	97	0.17
14	0.1	DMF	103	0.22	103	0.15
15	0.5	DMF	80	0.18	77	0.17
16	0.5	DMF	97	0.30	95	0.30
17	0.1	DMF	68	0.10	44	0.08

EXAMPLE 22

A photographic developer, having the same composition as that described in example 19, was divided into more parts. A part was used without any further addition, the others were added with the quantities specified in table 5 of the new antifoggants of the present invention. Samples of the 3M Medical X-Ray Type R film of the applicant were exposed to the blue light of a tungsten lamp and then developed for 24 seconds at 35°C in the prepared developing baths. After development, the material was then fixed in a bath having the same composition as that used in example 19 and washed for a total processing time of 90 seconds. The samples, thus obtained, were then read at a densitometer. The results thereof are shown in table 5.

TABLE 5

Compounds	g/l developer	Fog	Relative Sensitivity
—	—	2.02	100
1	0.22	1.17	77
2	0.10	1.53	66
3	0.056	1.54	67
6	0.18	1.68	68
7	0.12	1.27	80
11	0.60	0.72	102
15	0.60	0.58	92
17	0.26	0.48	92

The compounds can be introduced into the bath by using a solvent, as in the case of introduction into the emulsion, or not.

The silver halide photographic emulsions of the present invention are silver chloride, silver bromide and silver iodide emulsions and mixtures thereof such as, for example, silver bromoiodide and silver chlorobromide iodide.

Such emulsions may include synthetic polymeric gelatin substitutes or additives, such as dextrane, polyvinyl alcohol, polyvinyl pyrrolidone, partially hydrolyzed polyvinyl acetate, polyethylacrylate, polymethylmethacrylate, polyamides, etc. The emulsions of the invention may be chemically sensitized with naturally active gelatine, by addition of chemical sensitizers such as thiourea, allylthiourea, thiocyanates, thiosulphates, etc. Sensitization may be effected by the addition of noble metals, such as gold salts. Spectral sensitizers may be employed in emulsions of the invention, such as cyanine and merocyanine dyes. Moreover, the emulsions of the invention may include such additives as color couplers, filtering dyes, surfactants, hardeners, stabilizers, additional fog restrainers, plasticizers, anti-oxidizing agents, developing accelerators, etc. A photographic element comprises one support such as polyester, cellulose acetate, and the like and at least one layer including a silver halide emulsion layer of the above described type coated thereon. Such element can additionally contain other layers, that is, protective layers, interlayers, antihalo layers, filter layers, etc.

The guanazyl and guanazylium salt compounds of the invention may be conveniently introduced in the form of solutions into emulsions or any other coating composition during preparation thereof. Although it is gener-

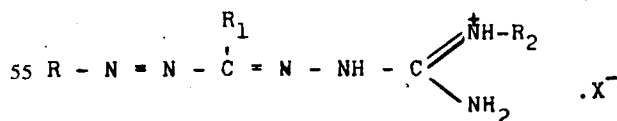
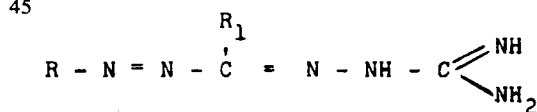
ally preferred to incorporate the guanazyl and guanazylium salt compounds of the invention directly into emulsion layers, these compounds may also be incorporated into layers adjacent the emulsion layers so that the silver halide emulsions are again in reactive association therewith. The guanazyl and guanazylium salt compounds are preferably introduced into photographic elements reactively associated with the silver halide emulsions in amounts ranging from about 0.05 to 2 mM/M of silver halide and most preferably from 0.1 to 0.5 mM/M of silver halide.

The processing baths of the present invention, as noted previously, may be photographic pre-baths, such as those known to the art to be useful prior to treatment of a silver halide photographic element with a developing solution. Predevelopment baths are usually (but not necessarily) acidic and may contain hardeners such as aldehydes and the like. The guanazyl and guanazylium salt compounds of the invention may, of course, also be employed in developing baths. Such baths are normally alkaline and include one or more silver halide photographic developing agents such as hydroquinone, metol, metol-hydroquinone, phenidone, hydroquinone-phenidone, and various p-phenylene diamine materials, the latter being useful in color development processes. The processing baths of the invention (prebaths and developer baths) preferably include from about 0.05 to 1 mM liter of solution. The guanazylium salt compounds are most preferably included in quantities ranging about from 0.1 to 1 mM liter of solution.

I claim:

1. A silver halide photographic emulsion having in reactive contact therewith at least a fog-inhibiting amount of a guanazyl and/or guanazylium salt compound.

2. A silver halide photographic emulsion having in reactive contact therewith at least a fog-inhibiting amount of a guanazyl and/or guanazylium salt compound respectively corresponding to the formulas:



wherein

R is an aryl group;

R₁ is an aryl group or a heterocyclic group;

R₂ is an alkyl group or hydrogen; and

X is an anion.

3. The emulsion of claim 2 wherein said anti-fogging compound is 1-3-diphenyl-guanazyl.

4. The emulsion of claim 2 wherein said anti-fogging compound is 1-(m-trifluoromethyl-phenyl)-3-phenyl-guanazyl.

5. The emulsion of claim 2 wherein said anti-fogging compound is 1-(p-chlorophenyl)-3-phenyl-guanazyl.

6. The emulsion of claim 2 wherein said anti-fogging compound is 1-phenyl-3(p-tolyl)-guanazyl.

7. The emulsion of claim 2 wherein said anti-fogging compound is 1-(p-tolyl)-3-phenyl-guanazyl.

8. The emulsion of claim 2 wherein said anti-fogging compound is 1-phenyl-3(o-chloro-phenyl)-guanazyl.

9. The emulsion of claim 2 wherein said anti-fogging compound is 1-phenyl-3-(p-nitro-phenyl)-guanazyl.

10. The emulsion of claim 2 wherein said anti-fogging compound is 1-(m-nitro-phenyl)-3-phenyl-guanazyl.

11. The emulsion of claim 2 wherein said anti-fogging compound is 1-3-diphenyl-guanazylium-chloride.

12. The emulsion of claim 2 wherein said anti-fogging compound is 1-3-diphenyl-guanazylium iodide.

13. The emulsion of claim 2 wherein said anti-fogging compound is 1-3-diphenyl-N-methyl-guanazylium-iodide.

14. The emulsion of claim 2 wherein said anti-fogging compound is 1-(p-chlorophenyl)-3-phenyl-guanazylium-pyrate.

15. The emulsion of claim 2 wherein said anti-fogging compound is 1-phenyl-3-(o-chlorophenyl)-guanazyli-

um-pyrate.

16. The emulsion of claim 2 wherein said anti-fogging compound is 1-(m-trifluoromethyl)-3-phenyl-guanazylium-pyrate.

17. The emulsion of claim 2 wherein said anti-fogging compound is 1-3-diphenyl-guanazylium-pyrate.

18. The emulsion of claim 2 wherein said anti-fogging compound is 1-(p-chloro-phenyl)-3-phenyl-N-methyl-guanazylium-iodide.

19. The emulsion of claim 2 wherein said anti-fogging compound is 1-phenyl-3-(pyridin)-guanazylium chloride.

20. A silver halide photographic element having a silver halide emulsion layer and a fog-inhibiting amount of a guanazyl and/or guanazylium salt compound in reactive association therewith.

21. A silver halide photographic element having a silver halide emulsion layer and a fog-inhibiting amount of a guanazyl and/or guanazylium salt compound of formulas respectively corresponding to those of claim 2 in reactive association therewith.

22. The photographic element of claim 21 wherein said guanazyl and/or guanazylium salt compound is included in said emulsion layer.

23. The photographic element of claim 21 wherein said guanazyl and/or guanazylium salt compound is included in a layer adjacent said silver halide emulsion layer.

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