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[54] **PHOTOGRAPHIC OVERCOAT COMPRISING A
BENZOTRIAZOLE TONING AGENT AND A
SILVER SALT OF 5-MERCAPTO-1-SUBSTITUTED
TETRAZOLE**
11 Claims, No Drawings

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G03c 7/00, G03c 1/72
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[56] **References Cited**
UNITED STATES PATENTS
2,403,927 7/1946 Kendall 96/109
2,573,027 10/1951 Kendall 96/52
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ABSTRACT: A photographic element comprising a support, a photographic silver salt layer and a layer comprising a binder, and the combination of triazole cold toning agent and a silver salt of a mercaptoazole, especially in an overcoat layer of such element, provides improved antiplumming and image tone. A combination of a benzotriazole and a silver salt of a 1-phenyl-5-mercaptotetrazole provides very cold tone images after hot glazing without loss of desired sensitometric properties.

PHOTOGRAPHIC OVERCOAT COMPRISING A BENZOTRIAZOLE TONING AGENT AND A SILVER SALT OF 5-MERCAPTO-1-SUBSTITUTED TETRAZOLE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to photographic materials, their preparation and use. One aspect of the invention relates to photographic elements comprising in combination a triazole cold toning agent and a silver salt of a mercaptotetrazole. Another aspect relates to a hydrophilic coating, especially an overcoat layer of a photographic element, containing such combination of materials. A further aspect relates to a process including the steps of developing a latent image in a photographic element, fixing or stabilizing the resulting image, and heat treating the resulting element employing in the photographic element, a combination of a triazole cold toning agent and a silver salt of a mercaptotetrazole, such as a silver salt of phenylmercaptotetrazole. The described photographic elements, coatings and processes of the invention provide improved resistance to plugging and bronzing of developed images.

2. Description of the Prior Art

In the photographic art many compounds have been proposed as additives to hinder or prevent "plugging" or "bronzing." These compounds are commonly known as antiplugging or antibronzing agents and are employed to reduce or prevent the degradation in a developed photographic image, which can occur when a photographic image is subjected to a heat treatment such as a hot-glazing treatment or hot-ferrotyping treatment. The common practice of hot glazing photographic prints, for example, tends to change the tone of the image undesirably providing a poor quality tone. This is known in the art as described, for example, in U.S. Pat. No. 2,403,927—Kendall, Fry, and Brooks issued July 16, 1946; British Pat. No. 794,680 issued May 7, 1958. U.S. Pat. No. 2,432,506—Chilton, Kendall and Phillips issued Dec. 16, 1947; and U.S. Pat. No. 2,432,864—Dimsdale and Robinson issued Dec. 16, 1947.

Heat treatment of photographic elements such as hot-glazing photographic prints tends to not only provide poor image tone but also tends to reduce maximum density with other undesired sensitometric characteristics. Various agents have been added to layers of photographic elements to produce a cold tone image without producing loss of photographic speed and without loss of maximum density. For instance, in the past free 5-mercaptotetrazoles have been added to photographic emulsions in an attempt to provide reduced plugging or bronzing, as described, for example, in U.S. Pat. No. 2,403,927 of Kendall, Fry and Brooks issued July 16, 1946. However, it was found that the presence of free 5-mercaptotetrazole is undesirable in either a photographic emulsion itself where its presence tends to adversely affect photographic speed or in, for example, an activator bath employed for processing where its presence tends to adversely effect contrast of the desired image. British Pat. No. 1,004,302 issued Sept. 15, 1965 indicates that it is desirable to employ a 5-mercaptotetrazole in the form of a silver salt to overcome these disadvantages. While addition of a silver salt of, for example, phenylmercaptotetrazole can have advantages, it often does not provide the desired cold tone image. This is demonstrated in following comparative examples 1 and 3.

On the other hand, triazoles have been employed in layers of photographic elements as antifoggants and cold toning agents. Often, however, it has been found that such triazoles provide undesired decrease in photographic speed and decrease in desired maximum density. This is also illustrated in the following comparative examples 1 and 3.

Accordingly, there has been a need for a photographic element, especially a photographic paper, which provides resistance to plugging and bronzing, but which also provides desired photographic speed without loss of maximum density or other desired sensitometric properties and which has desired very cold tone.

It is an object of the invention to provide a photographic element employing a combination of a triazole cold toning agent, especially a benzotriazole, and a silver salt of a mercaptoazole, which has resistance to plugging and bronzing without loss in photographic speed and without loss in maximum density.

Another object of the invention is to provide a hydrophilic coating containing the described combination of a triazole cold toning agent and a silver salt of a mercaptoazole, which provides the desired very cold tone without photographic speed loss and without loss of maximum density employed, for example, as an overcoat of a photographic element.

A further object of the invention is to provide a process of developing and fixing followed by a heat treatment, such as hot glazing of a photographic element using a combination of the described triazole cold toning agent and a silver salt of a mercaptoazole.

SUMMARY OF THE INVENTION

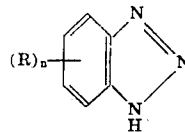
According to the invention, resistance to bronzing and/or plugging of a developed image can be provided without loss in photographic speed and without loss in maximum density by a photographic element, and process employing such element, comprising a support, a photographic light-sensitive silver salt layer, and a layer comprising a binder, (a) a triazole cold-toning agent and (b) a silver salt of a mercaptoazole. A hydrophilic layer of a photographic element comprising the described combination of a triazole cold toning agent and a silver salt of a mercaptoazole, especially an overcoat layer of a photographic element containing the described combination, can provide the described combination of advantages. A photographic element, as described, comprising a support, a photographic silver salt layer and an overcoat layer comprising 1,2,3-benzotriazole and a silver salt of 1-phenyl-5-mercaptotetrazole has been found especially suitable.

If the described triazole cold toning agent is employed in a photographic silver salt layer and the described silver salt of mercaptoazole is employed in, for example, an overcoat layer, a speed loss is obtained even though desired very cold tone is achieved. This is demonstrated in following comparative example 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Accordingly, one embodiment of the invention comprises a photographic element comprising a support, a photographic silver salt layer, and a layer comprising a binder, (a) triazole cold toning agent and (b) a silver salt of a mercaptoazole.

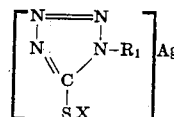
A range of triazole cold toning agents can be employed in the described combination of the invention. Any of those employed for cold toning purposes can be employed according to the invention. A suitable triazole cold toning agent, for example, includes a benzotriazole, such as 1,2,3-benzotriazoles of the formula:



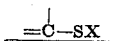
wherein R is hydrogen or alkyl, such as alkyl containing one to five carbon atoms, including methyl, ethyl, propyl, butyl and pentyl.

Examples of suitable triazole cold toning agents include benzotriazole, methyl benzotriazole, and ethyl benzotriazole.

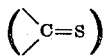
Also a range of silver salts of mercaptoazoles can be employed. A suitable silver salt of a mercaptoazole includes a silver salt of a 5-mercaptotetrazole, such as a silver salt of a 5-mercaptotetrazole of the formula:



wherein R₁ is an aliphatic or aromatic hydrocarbon radical containing one to 3 carbon atoms and SX is a mercapto function or group. R₁ can be, for example, alkyl containing one to three carbon atoms, typically one to five carbon atoms, for example, methyl, ethyl, propyl, butyl and pentyl or aryl containing six to 20 carbon atoms, such as phenyl, tolyl, xylyl and naphthyl. In addition, many of the mercaptotetrazole compounds can be in the tautomeric form, for example, in the thione form, in which case the labile hydrogen atom in the mercapto function is bonded to the nitrogen atom and the



group becomes a thiocarbonyl group



5-mercaptotetrazole, as employed herein, includes compounds in which the mercapto function is in any of these forms. Suitable atoms or groups which R₁ can contain together with hydrogen and carbon include, for example, alkoxy, phenoxy, halogen, for example, chlorine, bromine and iodine, cyano, nitro, amino, substituted amino, such as alkyl amino containing one to five carbon atoms, methyl amino, ethyl amino and dimethyl amino, sulfo, sulfonyl, sulfamyl, sulfonylphenyl, sulfonylalkyl, for example, sulfonylalkyl containing one to five carbon atoms, such as sulfonylmethyl, sulfonylethyl and sulfonylpentyl, sulfoamidoalkyl, for example, sulfoamidoalkyl containing one to five carbon atoms, carboxy, carboxylate, carbamyl, carbamylphenyl, carbamylalkyl, for example, carbamylalkyl containing one to five carbon atoms, such as carbamylmethyl, carbamylethyl and carbamylpentyl. The mercapto function or group can be in the free —SH form or in the salt form —SZ where Z is a cation, excluding hydrogen, for example, an alkali metal, such as sodium or potassium, or ammonium ion.

Especially good results have been obtained according to the invention employing a photographic element comprising a support, a photographic silver salt layer and an overcoat layer comprising 1,2,3-benzotriazole and a silver salt of 1-phenyl-5-mercaptotetrazole.

A range of concentrations of the described combination of a triazole cold toning agent and a silver salt of a mercaptoazole can be employed according to the invention. The most suitable concentration will depend on the desired image tone, the concentration of other components, the particular photographic silver salt employed, processing conditions and the like.

Typically a concentration of about 0.1 to about 10 milligrams per square foot of the photographic element of the described triazole cold toning agent and a concentration of about 10 to about 70 milligrams per square foot of the photographic element of the described silver salt of a mercaptoazole is suitable. For instance, employing a photographic element comprising a support, a photographic silver halide layer, typically a photographic silver halide gelatino emulsion layer and a hydrophilic overcoat layer, typically a gelatino overcoat layer, a concentration of 0.1 to about 10 milligrams per square foot of 1,2,3-benzotriazole and about 10 to about 70 milligrams per square foot of the silver salt of 1-phenyl-5-mercaptotetrazole is suitable.

A wide range of photographic silver salt developing agents can be employed for developing an image in a photographic element of the invention. These include any of those commonly employed in the photographic art such as, for example, polyhydroxybenzenes such as hydroquinone developing agents including hydroquinone, alkyl substituted hydroquinone, e.g., t-butylhydroquinone, methylhydroquinone, dimethylhydroquinone; catechol and pyrogallol; chlorosubstituted hydroquinones, such as chlorohydroquinone or dichlorohydroquinone; alkoxy substituted hydroquinone such as methoxy or ethoxy hydroquinone; aminophenol developing agents, such as N-methyl-p-aminophenol and 2,4-

diaminophenols including their acid salts; ascorbic acid developing agents; 3-pyrazolidone developing agents including those described in British Pat. No 958,678 and British Pat. No. 930,572 such as 1-phenyl-3-pyrazolidone or 4,4-dimethyl-1-phenyl-3-pyrazolidone; acyl derivatives of p-aminophenols and the like. Such developing agents can be used alone or in combination.

One or more of the described developing agents can be employed in a photographic element of the invention. For example, a developing agent can be present in an overcoat layer containing the described combination of a triazole cold toning agent and a silver salt of a mercaptoazole. A typical photographic element according to this embodiment is a support comprising a photographic silver halide layer and a layer, typically an overcoat layer, comprising a photographic silver salt developing agent, a triazole cold toning agent such as benzotriazole, and a silver salt of a mercaptoazole, such as a silver salt of 1-phenyl-5-mercaptotetrazole.

The described photographic elements of the invention can also contain free mercaptoazole such as 1-phenyl-5-mercaptotetrazole if desired. Presence of free mercaptoazole in a photographic emulsion as compared to another layer of the described photographic element can cause undesired effects, however, such as reduction of photographic speed. Therefore, it is often preferable to avoid presence of free mercaptoazole in the photographic layers described.

While silver salts of mercaptoazoles are preferred according to the invention, other soluble metal salts of mercaptoazoles can be employed if desired. For example, silver salts and/or other soluble metal salts of mercaptotetrazoles as described in U.S. Pat. No. 2,432,867; 2,432,865; and 2,432,684 of Dimsdale et al. issued Dec. 16, 1947 can be employed. These include, for example, copper, gold, mercury, cadmium, zinc, nickel and the like. Silver, however, is preferred.

Another embodiment of the invention comprises a hydrophilic coating for a photographic element comprising a hydrophilic binder, a triazole cold toning agent as described, and a silver salt of a mercaptoazole also as described. A hydrophilic coating comprising a hydrophilic binder, benzotriazole and a silver salt of 1-phenyl-5-mercaptotetrazole has been found especially suitable. If desired this hydrophilic coating can also comprise an incorporated developing agent.

The various layers of photographic elements described according to the invention can be hardened with any suitable hardener, including for example, aldehyde hardeners, aziridine hardeners which are derivatives of dioxane, oxypolysaccharides such as oxystarch, as oxystarch, oxy plant gums and the like. The layers of the photographic element can contain hardeners such as alkali soluble bisulfite-aldehyde addition products which harden hydrophilic layers such as gelatin. Such hardeners can be incorporated into photographic emulsion layers or other layers of an element, particularly gelatin layers. Suitable alkali metal bisulfite-aldehyde addition products include, for example, sodium formaldehyde bisulfite, glutaraldehyde bis(sodium bisulfite), betamethyl glutaraldehyde bis(sodium bisulfite), maleic dialdehyde bis(sodium bisulfite) and the like.

Various colloids can be used alone or in combination as vehicles or binding agents in the photographic layers and elements employed according to the invention. A binding agent as employed herein includes any of such colloids. Among such materials are the natural and/or synthetic binding materials generally employed for this purpose in the photographic art including, for example, gelatin, colloidal albumin, water soluble vinyl polymers such as 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 water insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The photographic silver salts employed according to the invention include any of the photographic silver salts employed in the photographic art such as photographic silver halides, for example, silver bromide, silver iodide, silver chloride, mixed silver halides such as silver chlorobromide, silver bromoiodide and the like. Silver halides used can be those which form latent images predominately on the surface of the silver halide grains and those which form latent images inside the silver halide crystals as exemplified by U.S. Pat. No. 2,592,250 of Davey and Knott issued Apr. 8, 1952 as well as direct positive emulsions such as described in U.S. Pat. No. 2,541,472 of Kendall and Hill issued Feb. 13, 1951.

The photographic elements according to the invention can employ a wide variety of supports. Typical flexible supports include those generally employed for photographic elements such as cellulose nitrate film, cellulose acetate film, polyvinylacetate film, polystyrene film, polyethylene terephthalate film and related films or resinous materials as well as glass, paper and metal supports. Supports such as papers which are partially acetylated and/or coated with baryta and/or coated with a resin, such as an olefin polymer particularly a polyethylene, polypropylene, or ethylene-butene copolymer and the like give good results.

The photographic layers and elements of the invention can 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, and polyalkylene glycol derivatives, onium salts and thio ethers, plasticizers, coating aids such as anionic, nonionic and amphoteric surfactants and the like. The photographic emulsions disclosed herein can also be chemically sensitized with the compounds of the sulfur group such as sulfur, selenium and tellurium sensitizers, noble metal salts such as gold, or reduction sensitized with reducing agents or combinations of such materials. The photographic elements can also contain fluorescent brighteners such as stilbenes, coumarines, benzothiazoles, benzoxazoles, imidazoles, and the like.

It is often advantageous to employ an antifoggant in the described photographic elements. Suitable antifoggants include organic antifoggants such as benzothiazolium salts, benzimidazoles, and the like as employed in combination with the described triazoles and silver salts of mercaptoazoles. An antifoggant can be present in processing compositions, such as developer solutions, employed for processing the described photographic elements if desired. Photographic elements and/or compositions employed for processing photographic elements according to the invention can contain an inorganic antifoggant such as potassium bromide, potassium iodide and/or sodium bromide. The concentration of antifoggant in either the photographic element processed or in the processing composition will vary depending upon the desired image tone, other components present, subsequent processing conditions and the like. Usually less than about 2 percent by weight, e.g., about 0.01 percent to about 2 percent by weight, antifoggant is suitable in a processing composition employed for processing photographic elements of the invention.

Another embodiment of the invention comprises in a photographic process including the steps of developing a latent image in a photographic element; fixing or stabilizing the resulting image; and heat treating the resulting developed image; the improvement comprising employing a photographic element which comprises a support, a photographic silver salt layer and a layer comprising a binder, (a) triazole cold toning agent, such as a 1,2,3-benzotriazole, as described and (b) a silver salt of a mercaptoazole, such as a silver salt of a 1-phenyl-5-mercaptotetrazole, as described.

Heat treating as described herein includes any suitable treatment of the described photographic elements at elevated temperatures, such as temperatures of about 50° C. to about 200° C. Such heat treatment can be carried out by passing the described photographic elements over a suitable heating means such as a heated plate for a short period such as a few seconds. Heat treating includes, for example, ferrotyping and/or hot glazing known in the photographic art.

Developing the described latent image in a photographic element of the invention and fixing or stabilizing the resulting image can be carried out employing any of the developer compositions, fixing or stabilizing compositions, commonly employed in the photographic art. A typical process according to the invention comprises developing a latent image in a photographic element as described by immersing or otherwise contacting the described photographic element with the developer composition such as the one containing a silver halide developing agent, sodium sulfite, a development activator, and potassium bromide, and then fixing the resulting image employing an aqueous fixing solution such as Kodak F-5 Fixer which is an aqueous solution of sodium thiosulfate, sodium sulfite, acetic acid, boric acid and potassium alum. After fixing or stabilizing the resulting image, it can be heat treated by drying at elevated temperatures such as at approximately 60° C. to about 100° C. employing a suitable photographic element dryer such as a Kodak Gloss Print Dryer.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

This is a comparative example.

A photographic silver chloride gelatin emulsion is coated on a baryta coated paper support at the rate of 42 milligrams of silver per square foot and 506 milligrams of gelatin per square foot. A gelatin layer is coated over the resulting emulsion at the rate of 102 milligrams of gelatin per square foot. The resulting photographic element is designated as sample 1A.

A photographic element is prepared the same as sample 1A with the exception that the gelatin overcoat layer contains 36.7 milligrams per square foot of the silver salt 1-phenyl-5-mercaptotetrazole. This sample is designated as sample 1B.

A third sample is prepared the same as sample 1A with the exception that 1.10 milligrams of 1,2,3-benzotriazole per square foot is added to the photographic emulsion layer. The resulting sample is designated as sample 1C.

Samples 1A, 1B and 1C are exposed sensitometrically and the resulting images are developed employing Kodak D72 Developer having the following composition:

N-methyl-p-aminophenol, sulfate	3.0 grams
sodium sulfite, desiccated 45.0 grams	
hydroquinone	12.0 grams
sodium carbonate, monohydrated	80.0 grams
potassium bromide	2.0 grams
water to make 1 liter	

The resulting image is fixed employing Kodak F-5 Fixer which has the following composition:

sodium thiosulfate	240.0 grams
sodium sulfite, desiccated	15.0 grams
acetic acid, 28%	48.0 cc.
boric acid	7.5 grams
potassium alum	15.0 grams
water to make 1 liter	

The resulting samples are washed with water and dried at approximately 87° C. employing a print drier (Kodak Gloss Print Drier). Resulting relative speed, contrast, maximum density and image tone are set out in the following table I in example 2.

EXAMPLE 2

A photographic element according to the invention is prepared the same as sample 1A of example 1 with the exception that 36.7 milligrams per square foot of the silver salt of 1-phenyl-5-mercaptotetrazole (PMT), and 1.13 milligrams per square foot of 1,2,3-benzotriazole is employed in the described gelatin overcoat layer. The resulting photographic element is exposed sensitometrically and processed as described in example 1. The results are set out in the following table I: 10

TABLE I

Example	Relative speed	Contrast	D_{max}	Image Tone		
				Density at		Tone
				460 $m\mu$	650 $m\mu$	
1A (Prior art—control gelatin overcoat) . . .	100	1.50	1.43	.169	.167	Neutral.
1B (Prior art—silver salt of PMT)	100	1.65	1.74	.158	.149	Cold.
1C (Benzotriazole)	63	1.45	1.38	.170	.170	Neutral to cold.
2 (Invention—combination)	89	1.53	1.71	.170	.148	Very cold.

The results set out in table I demonstrate that the combination according to the invention provides the desired very cold tone without undesired loss of relative speed, contrast, and maximum density. In comparison when the silver salt of 1-phenyl-5-mercaptotetrazole is employed in the coating over an emulsion layer (sample 1B) in the absence of a triazole cold toning agent, e.g., 1,2,3-benzotriazole, the desired very cold tone is not achieved. On the other hand 1,2,3-benzotriazole in the absence of a silver salt of 1-phenyl-5-mercaptotetrazole (sample 1C) provides undesired decrease in relative speed, and does not provide the desired very cold tone.

EXAMPLE 3

This is a further comparative example.

A photographic element is prepared the same as sample 1A as described in example 1. This is designated as sample 3A and is employed as a control.

Another sample is prepared the same as sample 1A as described in example 1 with the exception that 1.90 mg./ft.² of 1,2,3-benzotriazole is added to the described gelatin overcoat. The resulting sample is designated as sample 3B.

A third sample is prepared the same as sample 1A as described in example 1 with the exceptions that 2.08 mg./ft.² of 1,2,3-benzotriazole is added to the described photographic emulsion layer; 44.3 mg./ft.² of the silver salt of 1-phenyl-5-mercaptotetrazole is added to the described gelatin overcoat layer.

The resulting samples are exposed sensitometrically and processed as described in example 1. The results are set out in table II in following example 4

EXAMPLE 4

A photographic element is prepared the same as sample 1A described in example 1 with the exception that the described gelatin overcoat contains 38.5 mg./ft.² of the silver salt of 1-phenyl-5-mercaptotetrazole and 1.10 mg./ft.² of 1,2,3-benzotriazole.

The resulting photographic element is processed as described in example 1 and the results are set out in table II.

TABLE II

Example or sample No.	Relative speed	Contrast	Image tone				Variation
			D_{max}	Density at—		Tone	
				460 $m\mu$	650 $m\mu$		
3A.....	100	1.38	1.73	0.152	0.148	Neutral.	All gelatin overcoat.
3B.....	74	1.42	1.69	0.164	0.148	Cold.....	Gelatin overcoat containing benzotriazole.
3C.....	58	1.37	1.76	0.164	0.144	Very cold.	Gelatin overcoat containing silver salt of 5-mercaptotetrazole; emulsion layer containing benzotriazole.
4.....	74	1.40	1.75	0.164	0.145	ery cold	Gelatin overcoat containing silver salt of 5-mercaptotetrazole and benzotriazole (invention).

The results in table II demonstrate that desired very cold tone without undesired loss in relative speed or undesired loss

in maximum density is obtained only in the case of the photographic element of the invention, i.e., example 4 compared to samples 3A, 3B and 3C. While sample 3C containing no benzotriazole in the overcoat layer provides desired very cold tone, a significant loss in relative speed is observed. Sample 3B provides undesired loss in maximum density and lacks desired very cold tone.

EXAMPLE 5

Similar results are obtained as in example 4 when methylbenzotriazole is employed in place of benzotriazole.

A photographic element can be prepared as described employing a thiohydantoin cold tone, such as a 5,5-dialkyl-4-thiohydantoin, in place of the triazole cold toning agent. For instance, a photographic element can be prepared employing a paper support, a photographic silver halide emulsion coating and a gelatin overcoat containing, in combination, a silver salt of 1-phenyl-5-mercaptotetrazole and 5-ethyl-5-methyl-4-thiohydantoin. Upon exposure and processing as described in example 1, a good image is produced.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A photographic element comprising a support, a photographic, light-sensitive silver salt layer and an overcoat layer comprising a binder,

a. a benzotriazole cold toning agent, and

b. a silver salt of a 5-mercapto-1-substituted-tetrazole compound

2. A photographic element as in claim 1 comprising a support, a photographic silver salt layer and an overcoat layer containing 1,2,3-benzotriazole and a silver salt of 1-phenyl-5-mercaptotetrazole.

3. A photographic element as in claim 1 wherein said benzotriazole cold toning agent is present in a concentration of about 0.1 to about 10 milligrams per square foot and said silver salt of a 5-mercapto-1-substituted-tetrazole is present in a concentration of about 10 to about 70 milligrams per square foot.

4. A photographic element as in claim 1 comprising a support, a photographic silver halide layer and a gelatin overcoat layer comprising about 0.1 to about 10 milligrams per square foot of 1,2,3-benzotriazole and about 10 to about 70 milligrams per square foot of a silver salt of 1-phenyl-5-mercaptotetrazole

5. A photographic element as in claim 1 also comprising an incorporated developing agent.

6. A photographic element as in claim 1 also comprising an antifogant.

7. A hydrophilic coating as an overcoat layer for a photographic element comprising a binder, a benzotriazole cold toning agent, and a silver salt of a 5-mercapto-1-substituted-tetrazole compound.

8. A hydrophilic coating as in claim 7 comprising a binder, 1,2,3-benzotriazole and a silver salt of 1-phenyl-5-mercaptotetrazole.

9. A hydrophilic coating as in claim 8 also comprising an incorporated developing agent.

10. In a photographic process including the steps of developing a latent image in a photographic element; fixing or

stabilizing the resulting image; and heat treating the resulting element; the improvement wherein said photographic element comprises a support, a photographic light-sensitive silver salt layer and an overcoat comprising a binder,

a. benzotriazole cold toning agent, and

b. a silver salt of a 5-mercapto-1-substituted-tetrazole compound.

11. A process as in claim 10 wherein said heat treating comprises ferrotyping or hot glazing the resulting photographic element.

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