

[54] NOVEL COMPOSITIONS AND
PHOTOGRAPHIC PROCESSES

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96/111

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[57] ABSTRACT

Novel adducts are formed from a thioamine and glutaraldehyde. The adducts when incorporated in photographic processing compositions increase the efficiency of development of exposed silver salts.

10 Claims, 2 Drawing Figures

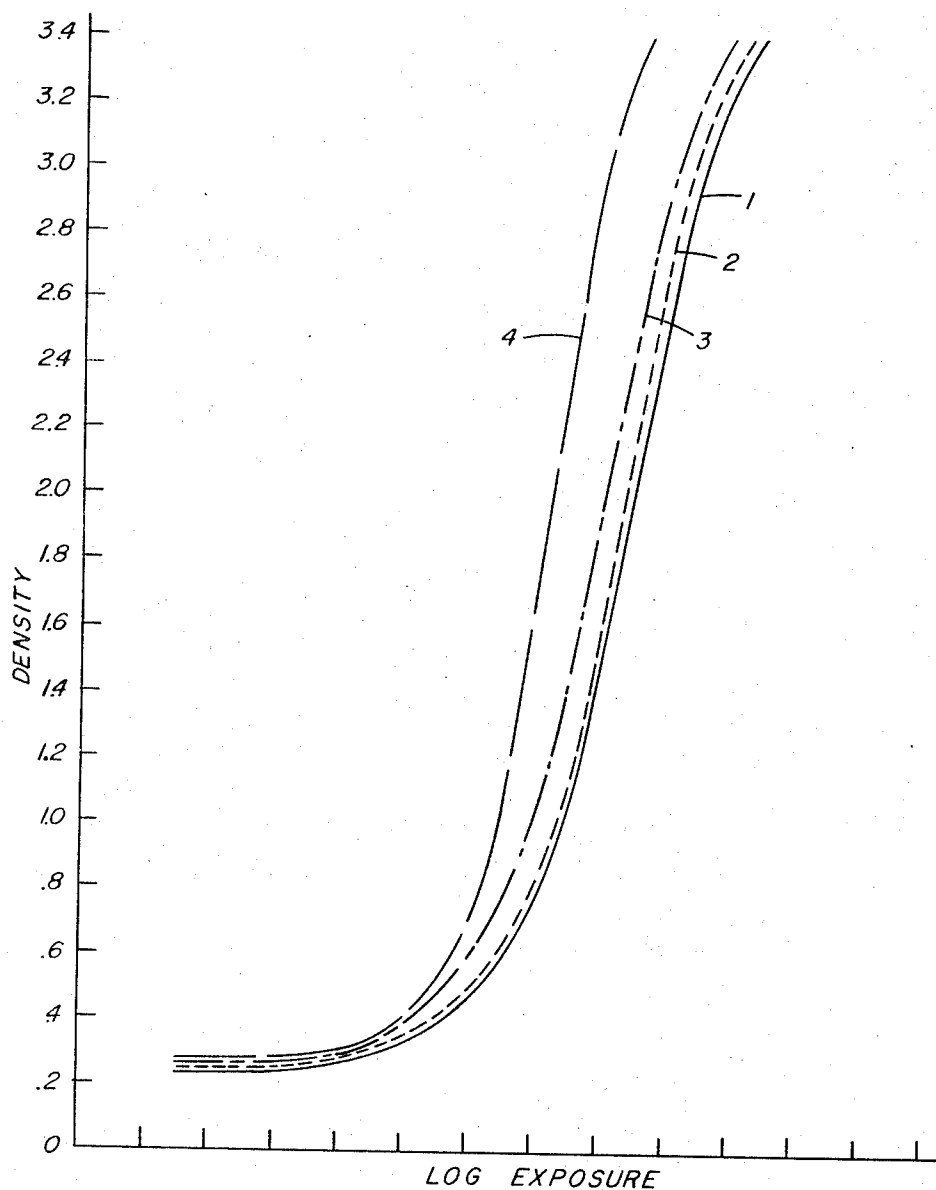
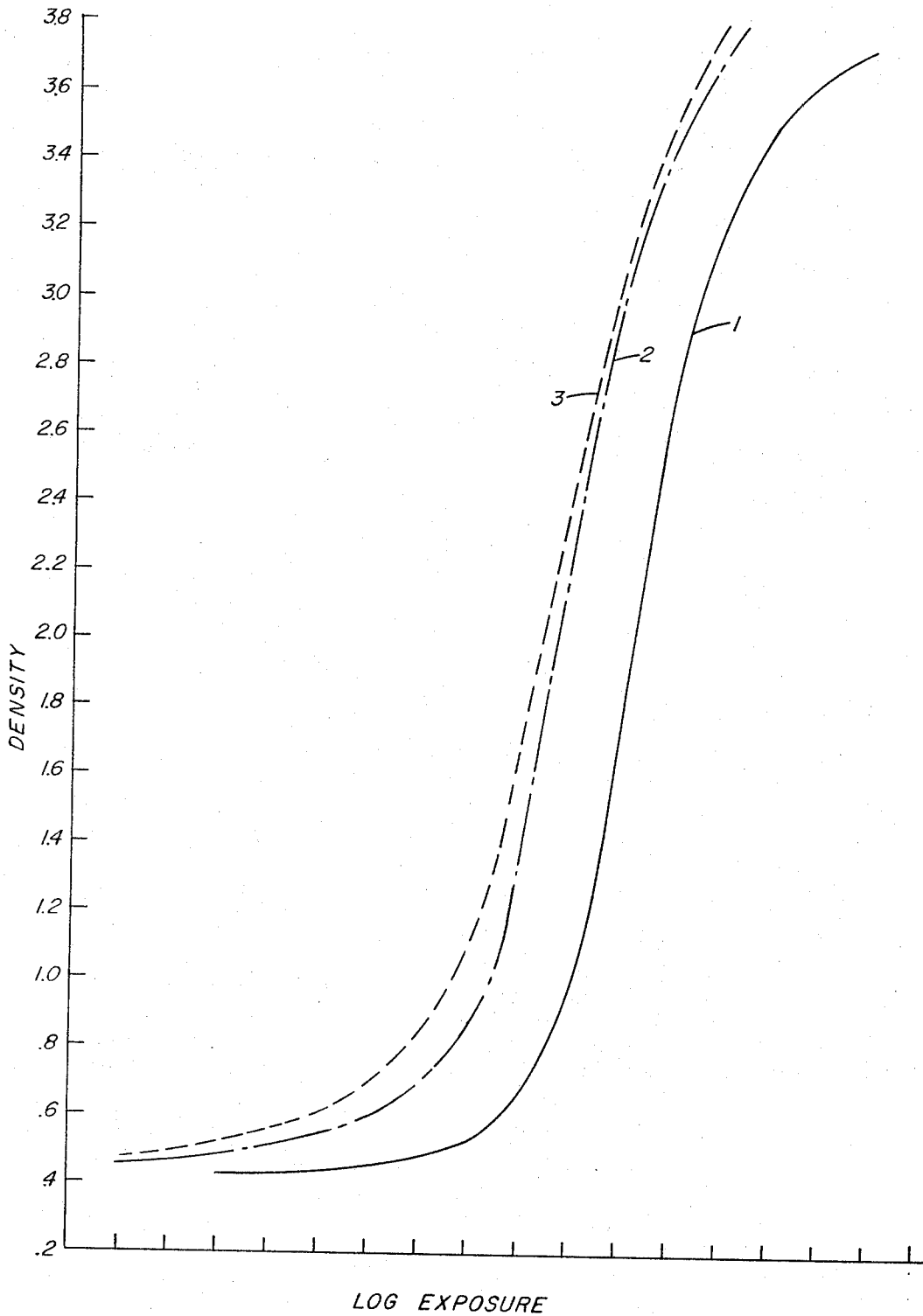


FIG. 1

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LOG EXPOSURE

FIG. 2

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NOVEL COMPOSITIONS AND PHOTOGRAPHIC PROCESSES

This is a division of U.S. Patent Application Ser. No. 104,690, filed Jan. 7, 1971.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to new compositions of matter, process of preparing such compositions, photographic processing compositions containing the novel compositions and to processes employing said processing compositions. In one aspect, this invention relates to a new composition of matter which is an adduct of a thioamine and glutaraldehyde. In another aspect, this invention relates to the methods of preparing the novel adducts. In yet another aspect, this invention relates to processes of developing exposed silver salts in a photographic element employing said processing composition.

2. Description of the Prior Art

The processing of photographic materials has for many years been performed by conventional processing methods such as tank and tray processing methods. The quality of the conventionally processed photographic material has generally been satisfactory. However, the processing time is generally long, that is, in the order of from 10 to 20 minutes.

In recent years, the use of roller transport systems have come into vogue. Through the employment of such transport systems the time of processing photographic elements has been reduced to minutes and often reduced to as short a time as below about a minute.

In attempts to further increase the speed of existing machine processes, such as by raising processing and drying temperatures, there is generally obtained a product which suffers from a substantial reduction in the sensitometric properties of the film. It is evident, therefore, that the art would greatly benefit should there be discovered a means of increasing the photographic speed of films, with respect to the processing of said films, without any substantial detrimental affects on the sensitometric properties such as, for example, a reduction in contrast or D_{max} . In the case of medical radiography, both an increase of speed and an improvement in D_{max} and contrast would greatly enhance the radiographic techniques as a diagnostic tool.

The increase in photographic speed with respect to development provides several degrees of freedom not ordinarily available, for example, one may decrease the silver halide coverage, the processing time of the exposed film can be decreased or with regard to radiography, the patient may be exposed to smaller amounts of radiation.

Although it is known to add either cysteine or aldehydes to photographic systems, i.e., photographic elements and photographic processing compositions, it has not been taught heretofore that one may incorporate the novel adducts of this invention into a photographic processing composition.

SUMMARY OF THE INVENTION

In accordance with this invention, there are provided photographic processing compositions which exhibit a marked increase in photographic speed accompanied by an improvement in sensitometric properties such as D_{max} and contrast. The photographic processing com-

positions of this invention contain, in addition to the well known ingredients, an adduct of a thioamine and glutaraldehyde. As used hereinafter, "thioamines" include derivatives thereof.

It is accordingly an object of this invention to provide means for increasing the photographic speed of electromagnetic radiation sensitive elements.

It is another object to improve the sensitometric properties of photographic elements.

It is another object to provide a new composition of matter which is an adduct of an aminothiols and glutaraldehyde.

It is still another object to provide means for preparation of the novel adducts. It is another object to provide photographic processing compositions containing the novel adducts.

Other objects of this invention will become obvious to those skilled in the art from that which follows:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with this invention, the above and other objects are attained by providing an adduct of a thioamine or derivative thereof with glutaraldehyde. The novel adducts so provided are incorporated in photographic processing compositions thereby significantly increasing the efficiency of the developers in developing exposed silver salts. Thioamine should be understood to be an amine compound containing a sulfur atom having an oxidation state of two. Illustrative of the thioamines which may advantageously be utilized are aminothiols, aminodisulfides and thiolactones.

The first of said compounds or their salts, preferably the hydrochloride salts, which are preferably employed in the formation of the adducts employed in this invention fall into two general classes. Compounds illustrative of Class I each contain at least one sulfur atom having an oxidation state of two, a carboxy group or its lactone, and an amino group. Compounds illustrative of Class I are cysteine or its homologues and other amino acids containing a sulfur atom having an oxidation state of two. Compounds of Class II contain an amino group, and a sulfur atom having an oxidation state of two. The following is an illustrative non-limiting list of the first compound suitable in forming the adducts of this invention:

Class I

L-cysteine . HCl,

L-cystine,

DL-penicillamine, and

DL-homocysteinethiolactone . HCl

Class II

2-aminoethanethiol . HCl

In a preferred aspect of this invention, the compounds employed in forming the adducts of this invention are those of Class I. In another preferred aspect cysteine, cystine, penicillamine, homocysteinethiolactone and 2-aminoethanethiol.HCl are utilized in forming the adduct. In yet another preferred aspect, cysteine is employed in forming the adduct.

The second of said compounds employed in the formation of the adducts employed in this invention is glutaraldehyde.

Illustrative of the adducts which may be employed in this invention are the products obtained by mixing: cysteine and glutaraldehyde, glutaraldehyde and DL-penicillamine, glutaraldehyde and DL-homocysteine-

thiolactone, glutaraldehyde and DL-methionine, glutaraldehyde and 2-aminoethanethiol. Preferred adducts are those formed from glutaraldehyde and one of L-cysteine.HCl, L-cystine, DL-penicillamine, DL-homocysteinethiolactone.HCl or 2-aminoethanethiol.HCl.

The adducts of this invention are easily prepared by merely adding glutaraldehyde to the thiamine or vice versa. The adduct can be formed in situ with respect to the processing composition or the adduct can be preformed and then added to the developer solution. It is generally more desirable to form the adduct first and then add it to the processing composition as compared to forming the adduct in situ with regard to the processing composition. The preferability of preforming the adduct is manifested through the additional speed increase observed over that obtained by in situ formation; however, the processing composition containing the adduct formed in situ evidences substantial improvements over the prior art. It should be understood, therefore, that the invention includes both preformed adducts and adducts formed by adding the compounds separately to the processing composition.

FIG. 1, which describes a characteristic H and D curve compares the density versus log exposure for emulsion processed in: a control developer solution (1), the same control developer solution to which glutaraldehyde has been added (2), the same control developer solution to which cysteine has been added (3), and the developer solution to which a preformed adduct has been added. A more detailed description of FIG. 1 is found in Example 3.

FIG. 2 which shows the characteristic H and D curves of density versus log exposure illustrates that both the processing solution (3) containing the preformed adduct and the processing solution (2) in which the adduct is formed in situ are superior to the processing solution (1) absent the adduct but otherwise identical. The processing solution containing the adduct clearly showed increased speed and contrast as manifested by the developed film as compared with the processing solution absent the adduct.

The adduct when preformed can be prepared under acid, neutral, or basic conditions. The solvent employed can be any in which both the first and second compound are soluble. A preferred solvent is water.

The adducts of this invention have been subjected to a thorough analytical investigation, however, the structure and composition remains indefinite. It is clear, however, that a novel composition is formed by the reaction of the first and second compounds as exemplified by Example 1. Table II, for example, illustrates the color changes over a period of time said color changing manifesting that a new product is being formed.

The adduct is readily soluble in highly acid and basic solutions, however, as the pH of the solution is made to approach neutrality the adduct precipitates out. The adduct can be added to the processing solution in any form, i.e., as a precipitate, as a basic solution or as an acid solution.

Some adduct is formed as soon as the two compounds are in contact, however, the longer the compounds are allowed to react the more adduct is formed. After as short a time as two hours of reaction, the obtained adduct substantially improved the photographic processing composition. After about 24 hours of reaction time, the adduct obtained causes a potent increase

in photographic speed with regard to the processing composition.

The photographic speed increases obtained in processing photographic materials in the presence of the adducts vary in relation to the amount of first compound (thioamine) employed in forming the adduct as well as the ratio of said first compound to said second compound (glutaraldehyde). Increases in the concentration of cysteine is accompanied by speed increases.

The useful ratios of first compound to second compound can vary over a wide range, said ranges being easily determined through routine experimentation. When, however, the adduct is employed in photographic processing compositions, the first compound should not be present in substantial excess over the second compound since a serious reduction in speed may be produced. As a general rule, the adduct can comprise a molar ratio of from about 4 to 1 to about 1 to 60 of said first compound to said second compound. A preferred molar ratio is from about 2 to 1 to about 1 to 8 of said first compound to said second compound. Another preferred range is from 1 to 1 to about 1 to 2 of said first compound to said second compound. Still another preferred ratio is about a 1 to 1 ratio of said first and second compound.

The adducts are not reducing agents for silver salts and therefore alone are not effective as photographic developing agents. It has been discovered, however, that when added to a photographic developing or processing composition, the developing activity of the composition is greatly enhanced. Without being bound by any theoretical explanation, it would appear that the adducts of this invention increase the efficiency of the developing power of the developing or processing composition.

The adducts of this invention extend broadly to all photographic developer and processing compositions. However, the novel developing or processing solutions, i.e., those solutions containing the novel adducts, are of greatest practical importance with respect to high speed materials such as radiographic materials, separation negative materials and the like. The compositions, in addition to containing a developing agent and the novel adducts can contain other ingredients employed in the processing of a photographic product, for example, stabilizer compositions, monobaths, activator compositions, hardener compositions and the like. Preferably, the adducts are employed in an aqueous alkaline developer solution.

The adduct concentration in the processing solutions can vary over a wide range. It has been discovered, however, that the sensitometric properties such as D_{max} and contrast as well as speed are improved with increasing concentration of the adduct. With each of the adducts there is a point at which increased concentration, for example 0.30 g/l based on said first compound, will produce an increase in fog, however, the increase in the fog level is readily counteracted through the use of antifoggants. Typical processing and developing solutions contain from about 0.05 g/l to about 0.50 g/l. A preferred concentration is from about 0.12 g/l to about 0.24 g/l. A preferred concentration is 0.12 g/l.

This invention can be further illustrated by the following examples of preferred embodiments thereof, and from the drawings, of which FIGS. 1 and 2 compares characteristic curves for processing compositions of this invention and for the prior art composition.

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

EXAMPLE 1

This example illustrates a preferred method of preparing the novel adducts of this invention.

To an aqueous solution at a pH of 1.4 is added 1 mole L-cysteine and 1 mole of glutaraldehyde. The solution is allowed to stand for 20 hours. Upon mixing the solution remains clear and colorless. After about 1 hour the solution begins to turn straw in color and thereafter gradually turns to an amber color. The adduct is precipitated out of solution by slowly raising the pH through the addition of pyridine.

Adducts are similarly prepared by mixing glutaraldehyde with cystine, penicillamine, homocysteinethiolactone, serine, methionine, alanine, proline, 3-mercaptopropionic acid or 2-aminoethanethiol. The adducts formed from serine, alanine, proline and 3-mercaptopropionic acid are readily formed; however, they appear not to have a significant affect on the photographic speed. The results with reference to color and the pH are summarized in Table II.

As will be seen in Table VI below, similar adducts show no utility and hence are not within the scope of this invention.

TABLE II

Compound, 1:1 M. with Glutaraldehyde	pH and Color at				
	Mixing	15 Minutes	1 Hour	4 Hours	20 Hours
L-Cysteine.HCl	1.4 clear	1.4 clear	1.25 straw	1.2 straw	1.2 amber
*L-Cystine (.5M Cystine: 1M GA)	3.1 milky	3.2 cloudy	3.25 cloudy	3.3 orange	3.3 orange
DL-Penicillamine	3.6 clear	3.3 straw	3.15 amber	3.15 amber	3.15 red
L-Homocysteinethiolactone.HCl	1.5 straw	1.3 amber	1.3 red	1.15 brown	1.15 black
L Serine	4.4 clear	4.4 clear	3.4 straw	3.5 straw	3.5 amber
DL-Methionine	4.3 straw	3.9 orange	3.9 orange	3.9 orange	3.9 tan pptd
DL-Alanine	4.25 straw	3.9 red	3.9 brown	3.9 brown	3.85 black
L-Proline	4.35 clear	4.35 clear	4.35 clear	4.35 clear	4.35 clear
3 Mercaptopropionic Acid	2.2 clear	2.2 clear	2.2 clear	2.2 clear	2.2 cloudy
2 Aminoethanethiol.HCl	2.35 clear	2.3 pale green	1.7 yellow	1.5 yellow	1.5 amber

*insoluble in H₂O at the pH of mixing

EXAMPLE 2

This example illustrates that the adduct which may be formed in situ produces photographic speed increases as a result of the photographic development process.

A developer solution (A) is prepared to contain:

1-Phenyl-3-pyrazolidone	1.5 g
Hydroquinone	30.0 g
Potassium sulfite 45 percent aqueous	90.0 ml
Potassium carbonate	10.0 g
5-Nitroindazole	0.25 g
5-Methyl benzotriazole	0.06 g
Potassium bromide	10.0 g
Sodium bisulfite	3.75 g
Glutaraldehyde 25 percent aqueous	18.6 ml
EDTA *	1.0 g
Water to	1.0 liter

pH 10.05

*Ethylenediamine Tetraacetic Acid

A developer solution (B) is prepared as in (A), but modified by the addition of 0.12 gram of cysteine.

A developer solution (C) is prepared as in (A) but modified by the addition of 0.24 gram of cysteine.

Separate sheets of a coarse-grained silver bromoiodide negative material of the type used in medical radiography is sensitometrically exposed and processed in a roller type processor at 95°C employing one of the above developers. The results are summarized in Table III:

TABLE III

Sensitometric Results					
Developer	Addend Cysteine Concentration	Fog	Relative Speed	Contrast	Dmax
A	(Control)	.18	1.00	2.60	3.44
B	0.12 g/liter	.18	1.30	2.68	3.52
C	0.24 g/liter	.20	1.70	2.8	3.58

The above data illustrate that at least 30% speed increase results from the presence of the cysteine, without significantly lowering the contrast or Dmax as often occurs with other speed increasing addenda.

EXAMPLE 3

This example illustrates the employment of the novel processing composition containing the preformed adducts.

A series of four high speed silver bromoiodide photographic emulsions are exposed and respectively tray processed in a typical high contrast photographic developing solution.

Developer 1 — Control Developer

1-Phenyl-3-pyrazolidone	1.5 g
Hydroquinone	30.0 g
Potassium sulfite 45 percent aqueous	90.0 ml
Potassium carbonate	10.0 g
5-Nitroindazole	0.25 g
5-Methyl benzotriazole	0.06 g
Potassium bromide	4.0 g
EDTA	1.0 g
Water to	1.0 liter

pH 10.05

Developer 2	— Control + 0.08 g/l of glutaraldehyde
Developer 3	— Control + 0.12 g/l of L-cysteine.HCl
Developer 4	— Control + preformed adduct of cysteine and glutaraldehyde

The samples are fixed, washed and dried in the conventional manner. The results are summarized in FIG. 1 and Table IV.

TABLE IV

Developer	Rel. Speed at 0.85 Above Fog
1	1.0
2	1.0
3	1.2
4	2.0

FIG. 1 shows the characteristic H and D curves of density versus log exposure for 25 seconds development time for each of the four processing compositions. Based upon the control (line 1) adding glutaraldehyde alone (line 2) produces essentially no increase in speed. L-cysteine added to a developer without glutaraldehyde (line 3) produces only a slight increase in speed. A substantial increase in speed and contrast is produced as shown by line 4 when the preformed adduct of L-cysteine.HCl and glutaraldehyde are added to the control processing composition. This amounts to a doubling of the photographic speed due to the particular developer solution.

EXAMPLE 4

This example illustrates that the concentration of the adduct as measured by the amount of first compound employed in the preparation of the adduct affects the speed.

Seven samples of a high speed silver bromide photographic emulsion are exposed and respectively tray processed in one of the processing solutions as summarized in Table V. These represent various amounts and ratios of cysteine and glutaraldehyde. The control solution is similar to the control in Example 3.

TABLE V

	millimoles/l LCH ^a	millimoles/l GA ^b	Rel. Speed (at 0.85 above fog)
Control	+	0	1.00
Control	+	1	1.50
Control	+	2	2.20
Control	+	1	1.35
Control	+	2	1.70
Control	+	4	1.50

^a L-cysteine.HCl

^b Glutaraldehyde

EXAMPLE 5

Several preformed adducts of glutaraldehyde and a compound listed in Table VI are prepared as in Example 1. The adducts so prepared include those of the invention and similarly formed compositions not within the scope of this invention.

Several high speed silver bromide emulsions are exposed and processed in the control developer employed as in Example 3 or in the developer which includes a preformed adduct. In each case, the adduct is formed from a 1 to 1 molar aqueous solution of first compound and second compound. The results are summarized in Table VI.

EXAMPLE 6

This example illustrates that the adducts which are useful in this invention should be formed from a compound which contains both a sulfur group and a nitrogen group such as aminoacids from protein hydroly-

sates, cysteine and aminoethanethiols whereas adducts formed from compounds not containing both a nitrogen group and a sulfur group do not contribute to a significant increase in the photographic speed. Thus, only minor increases are shown by the L-serine, DL methionine, DL-alanine, L-proline and 3-mercaptopropionic acid.

A speed increase during development in the presence of cysteine glutaraldehyde occurs with films sensitized to the infrared. Strips of such films after exposure are developed in a developer comprising:

TABLE VI

Compound Tested with Glutaraldehyde	Conc. Milli-mole/l of adduct in processing solution	Rel. Speed
Control	0	1.00
L-cysteine.HCl	1.0	1.51
L-cystine	0.5	1.23
DL-penicillamine	0.5	1.32
DL-homocysteinethiolactone.HCl	.12	1.59
L-serine	4	1.00
DL-methionine	4	1.07
DL-alanine	4	1.12
L-proline	4	1.02
3-Mercaptopropionic Acid	4	1.12
2-Aminoethanethiol.HCl	0.1	1.41

N-methyl-p-aminophenol sulfate	2.0 g
Hydroquinone	8.0 g
Sodium sulfite	90.0 g
Sodium carbonate	52.0 g
Potassium bromide	5.0 g
Water to	1.0 liter
Development was at 68° for 8 minutes	

The above solution is modified by the addition of 0.05 g cysteine hydrochloride and 0.05 g glutaraldehyde bisulfite. Exposed strips are developed as above. Sensitometric curves are plotted for the two sets of developed infrared films. A 0.10 speed increase is obtained for films developed in the developer containing the cysteine and the glutaraldehyde. The increase in speed also occurs over and above the normal increase in speed which results from known hypering treatments, as, for example, treatment with aqueous ammonium at about 45° for 40 seconds prior to exposure. In such cases, a total speed increase of 0.40 may result.

The silver halide layers which can be processed with the processing compositions of this invention can comprise silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. Suitable emulsions may be coarse or fine grain and can be prepared by any of the well-known procedures, e.g., single jet emulsions, double jet emulsions, such as Lippmann emulsions, ammonical emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264 issued Nov. 4, 1940; Illingsworth U.S. Pat. No. 3,320,069 issued May 15, 1967; and McBride U.S. Pat. No. 3,271,157 issued Sept. 6, 1966. Surface image emulsions may be used or internal image emulsions such as those described in Davey et al. U.S. Pat. No. 2,592,250 issued Apr. 8, 1952; Porter et al. U.S. Pat. No. 3,206,313 issued Sept. 14, 1965; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968 and Bacon et al. U.S. Pat. No. 3,447,927 issued June 3, 1969. If desired, mixtures of surface and internal image emulsions may be used as described in Luckey et al. U.S. Pat. No. 2,996,382 issued Apr. 15,

1961. Negative type emulsions may be used or direct positive emulsions such as those described in Leermakers U.S. Pat. No. 2,184,013 issued Dec. 19, 1939; Kendall et al. U.S. Pat. No. 2,541,472 issued Feb. 13, 1951; Berriman U.S. Pat. No. 3,367,778 issued Feb. 6, 1968; Schouwenaars British Pat. No. 723,019; Illingsworth et al. French Pat. No. 1,520,821; Ives U.S. Pat. No. 2,563,785 issued Aug. 7, 1951; Knott et al. U.S. Pat. No. 2,456,953 issued Dec. 21, 1968 and Land U.S. Pat. No. 2,861,885 issued Nov. 25, 1958. The emulsions may be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, Vol. 12, No. 5, Sept./Oct., 1964, pp 242-251.

The emulsions which are processed with the processing solutions of this invention may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. No. 1,623,499 issued Apr. 5, 1927; Waller et al. U.S. Pat. No. 2,399,083 issued Apr. 23, 1946; McVeigh U.S. Pat. No. 3,297,447 issued Jan. 10, 1967; and Dunn U.S. Pat. No. 3,297,446 issued Jan. 10, 1967.

The silver halide emulsions or layers which can be processed with the processing solutions of this invention may contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959; Dann et al. U.S. Pat. No. 3,046,134 issued July 24, 1962; Carroll et al. U.S. Pat. No. 2,944,900 issued July 12, 1960; and Goffe U.S. Pat. No. 3,294,540 issued Dec. 27, 1966.

The silver halide emulsions or layers which can be processed with the processing solutions of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al. U.S. Pat. No. 2,131,038 issued Sept. 27, 1938 and Allen et al. U.S. Pat. No. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. No. 2,886,437 issued May 12, 1959 and Heimbach et al. U.S. Pat. No. 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Pat. No. 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al. British Pat. No. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927 issued July 16, 1946; Kennard et al. U.S. Pat. No. 3,266,897 issued Aug. 16, 1966 and Luckey et al. U.S. Pat. No. 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Pat. No. 2,839,405 issued June 17, 1958; the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263 issued Aug. 28, 1951 and Yutzy et al. U.S. Pat. No. 2,597,915 issued May 27, 1952.

The photographic elements which are processed with the processing solutions of this invention may contain in place of or in combination with the developing agents present in the processing solution, incorporated

developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines. Combinations of developing agents can be employed in the practice of this invention. The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element. The developing agents may be added from suitable solvents or in the form of dispersions as described in Yackel U.S. Pat. No. 2,592,368 issued Apr. 8, 1952 and Dunn et al. French Pat. No. 1,505,778.

The processing solutions of this invention may be used in the development of elements designed for colloid transfer processes such as described in Yutzy et al. U.S. Pat. No. 2,716,059 issued Aug. 23, 1955, silver salt diffusion transfer processes such as described in Rott U.S. Pat. No. 2,352,014 issued June 20, 1944, and Land U.S. Pat. No. 2,543,181 issued Feb. 27, 1951, Yackel et al. U.S. Pat. No. 3,020,155 issued Feb. 6, 1962, and Land U.S. Pat. No. 2,861,885 issued Nov. 25, 1958; color image transfer processes such as described in Rogers U.S. Pat. Nos. 3,087,817 issued Apr. 30, 1963; 3,185,567 issued May 25, 1965; and 2,983,606 issued May 9, 1961; Weyerts et al. U.S. Pat. No. 3,253,915 issued May 31, 1966; Whitmore et al. U.S. Pat. No. 3,227,550 issued Jan. 4, 1966; Barr et al. U.S. Pat. No. 3,227,551 issued Jan. 4, 1966, Whitmore U.S. Pat. No. 3,227,552 issued Jan. 4, 1966; and Land U.S. Pat. Nos. 3,415,644; 3,415,645; 3,415,646 issued Dec. 10, 1968; and imbibition transfer processes as described in Minsk U.S. Pat. No. 2,882,156 issued Apr. 14, 1959.

The processing solutions of this invention can be used with elements designed for color photography, for example, elements containing color-forming couplers such as those described in Frohlich et al. U.S. Pat. No. 2,376,679 issued May 22, 1945, Jelley et al. U.S. Pat. No. 2,322,027 issued June 15, 1943; Fierke et al. U.S. Pat. No. 2,801,171 issued July 30, 1957, Godowsky U.S. Pat. No. 2,698,794 issued Jan. 4, 1966, Barr et al. U.S. Pat. No. 3,227,554 issued Jan. 4, 1966, and Graham et al. U.S. Pat. No. 3,046,129 issued July 24, 1962; or elements to be developed in solutions containing color-forming couplers such as those described in Mannes et al. U.S. Pat. No. 2,252,718 issued Aug. 19, 1941, Carroll et al. U.S. Pat. No. 2,592,243 issued Apr. 8, 1952; and Schwan et al. U.S. Pat. No. 2,950,970 issued Aug. 30, 1960; and in false-sensitized color materials such as those described in Hanson U.S. Pat. No. 2,763,549 issued Sept. 18, 1956.

The exposed silver halide emulsion can be either tray processed or machine processed in the presence of the processing solutions of this invention. In a preferred method a photographic element is machine processed whereby the element is processed in one continuous motion by transporting it into and out of at least one processing solution in the manner shown, for example, by U.S. Pat. Nos. 3,025,779 of Russell and Kunz issued Mar. 20, 1962; 3,078,024 of Sardeson issued Feb. 19, 1963; 3,122,086 of Fitch issued Feb. 25, 1964; 3,149,551 of Cramer issued Sept. 22, 1964; 3,156,173 of Meyer issued Nov. 10, 1964; and 3,224,356 of Fleisher and Hixon issued Feb. 21, 1965.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifica-

tions can be effected within the spirit and scope of the invention.

I claim:

1. A photographic developing composition comprising water, a silver halide developing agent and reaction products of a thioamine which is cysteine, cystine, DL-penicillamine, DL-homocysteinethiolactone or 2-aminoethanethiol with glutaraldehyde or with glutaraldehyde bisulfite in which said reaction products are obtained by reacting a mixture having a molar ratio of from about 4 to 1 to about 1 to 60 of said thioamine to glutaraldehyde or glutaraldehyde bisulfite.

2. A photographic developing composition of claim 1, in which said composition contains reaction products of cysteine and glutaraldehyde.

3. A photographic developing composition of claim 1 in which said reaction products are obtained by reacting a mixture having a molar ratio of from about 2 to 1 to about 1 to 8 of the said thioamine to glutaraldehyde.

4. A photographic developing composition of claim 1 in which said reaction products are obtained by reacting a mixture having a 1 to 1 molar ratio of said thioamine to said glutaraldehyde.

5. A photographic developing composition comprising water, a silver halide developing agent and reaction products of cysteine, with glutaraldehyde or with glutaraldehyde bisulfite in which said reaction products are obtained by reacting a mixture having a molar ratio

of from about 4 to 1 to about 1 to 60 of said cysteine to glutaraldehyde or glutaraldehyde bisulfite.

6. A method of developing an exposed photographic silver halide element which comprises treating an exposed silver halide layer with a photographic developing solution comprising water, a silver halide developing agent and reaction products of a thioamine which is cysteine, cystine, DL-penicillamine, DL-homocysteinethiolactone or 2-aminoethanethiol with glutaraldehyde or with glutaraldehyde bisulfite in which said reaction products are obtained by reacting a mixture having a molar ratio of from about 4 to 1 to about 1 to 60 of said thioamine to said glutaraldehyde or glutaraldehyde bisulfite.

7. A method of claim 6 in which said reaction products are of cysteine and glutaraldehyde.

8. A method of claim 6 in which said reaction products are obtained by reacting a mixture having about 4 to 1 to about 1 to 60 of said thioamine to glutaraldehyde.

9. A method of claim 6 in which said reaction products are obtained by reacting a mixture having a molar ratio of from about 2 to 1 to about 1 to 8 of said thioamine to glutaraldehyde.

10. A method of claim 6 in which said reaction products are obtained by reacting a mixture having a 1 to 1 molar ratio of said thioamine to said glutaraldehyde.

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