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# N,N-DISUBSTITUTED AMINO-METHYLTHIOCARBOXYLIC ACIDS AND USE THEREOF AS ANTIFOGGANTS IN PHOTOGRAPHIC EMULSIONS

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## ABSTRACT OF THE DISCLOSURE

N,N-disubstituted aminomethylthiocarboxylic acids, the preparation and use of such compounds as antifoggants and stabilizers for photographic elements and silver halide emulsions. Developing photographic elements in the presence of N,N-disubstituted aminomethylthiocarboxylic acids is also described.

## BACKGROUND OF THE INVENTION

### Field of the invention

This invention relates to new and improved antifoggants and stabilizers for photographic elements and to photographic silver halide emulsions containing said antifoggants and stabilizers therein. The invention also relates to a process of developing photographic elements in the presence of new and improved antifoggants.

### Description of the prior art

During development of a silver halide emulsion, small amounts of silver halide are reduced to metallic silver regardless of whether or not they have been exposed. This reduction of silver ion produces a background fog which is more specifically referred to as chemical fog.

Chemical fog, apparent in most silver halide systems, has been reduced by prior art methods of processing exposed silver halide material in the presence of compounds which restrict development of unexposed silver halide. Such compounds can be incorporated in the silver halide emulsion or in the processing solutions for developing such silver halide emulsions. Compounds which have been found to have a chemical fog inhibiting effect on emulsions which have been subjected to high temperature and high humidity conditions are referred to as emulsion stabilizers. On the other hand, compounds which have been found to have chemical fog inhibiting effects on emulsions which have not been exposed to adverse storage conditions are referred to as antifoggants. Although a large number of emulsion stabilizers and antifoggants have been used in the prior art, many of these compounds cause undesirable losses in emulsion speed and contrast and others lack adequate compatibility with emulsion gelatin.

## SUMMARY OF THE INVENTION

In accordance with this invention, there is provided a new class of compounds which are useful as antifoggants and stabilizers for photographic emulsions, viz. N,N-disubstituted aminomethylthiocarboxylic acids. These compounds may be represented by the general formula

$$\begin{matrix} R \\ | \\ N[CH_2-S-Y-COOH]_n \\ | \\ R_1 \end{matrix}$$

wherein $n$ is either 1 or 2 and, when $n$ is 1, R and $R^1$ may be alkyl (e.g. methyl, ethyl, octyl, etc.), cycloalkyl (e.g. cyclohexyl, cyclopentyl, etc.), aryl (e.g. phenyl, tolyl, naphthyl, etc.), or aralkyl (e.g. benzyl, phenethyl etc.) or when taken together with the nitrogen atom to which they are attached comprise a primary heterocyclic ring containing from 5 to 7 atoms in the ring to which may be fused another carbocyclic ring (e.g piperidino, morpholino, 3-azobicyclo [3·2·2]nonane-3-yl, etc.), and, when $n$ is 2, the group

$$\begin{matrix} R \\ | \\ N- \\ | \\ R_1 \end{matrix}$$

is the divalent piperazine radical

and Y is the radical remaining after the removal of the sulfhydryl group and a carboxyl group from a thiocarboxylic acid such as an alkylene group which may optionally be substituted with an alkyl, aryl, carboxyl or carboxyalkyl group (e.g., methylene, ethylene, propylene, ethylidene, carboxyethylene, etc.).

According to one embodiment of this invention, a fog-stabilizing amount of an N,N-disubstituted aminomethylthiocarboxylic acid is incorporated into the silver halide emulsion of a photographic element or in a layer contiguous to the silver halide emulsion. The N,N-disubstituted aminomethylthiocarboxylic acid stabilizes the emulsion against fog when the dried emulsion has been subjected to a prolonged high humidity and temperature incubation period without adversely affecting other sensitometric properties.

According to another embodiment of the invention, a photographic element comprising a support coated with at least one silver halide emulsion layer is developed in the presence of an N,N-disubstituted aminomethylcarboxylic acid. Preferably, this compound is present in the photographic element but it may be present elsewhere in the system—e.g., in the developer.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred groups of compounds of this invention which are particularly useful as antifoggants in photographic emulsions are those wherein the radical Y in the above general formula is one of the following groups: $(CH_2)_m$ wherein $m$ is an integer from 1 to 5 and, preferably, is 1 or 2;

$$\begin{matrix} COOH & \\ | & \\ -CH- & (CH_2)_n- \end{matrix}$$

wherein $n$ is an integer from 1 to 5 and, preferably, is 1; and

$$\begin{matrix} -CH- \\ | \\ (CH_2)_p \\ | \\ CH_3 \end{matrix}$$

wherein $p$ is an integer from 0 to 7 and, preferably is 0.

The novel compounds of this invention are prepared by reacting a thiocarboxylic acid with an N,N-disubstituted alkoxymethylamine in an appropriate solvent. Since the N,N-disubstituted aminomethylthiocarboxylic acids may exist as internal salts and the other products of the reaction are alcohols, it is preferable, for ease of isolation, that these compounds be prepared in a non-polar reaction solvent in which the internal salts are insoluble or only sparingly soluble and in which the alcohols which are also formed during the reaction are miscible. Examples of such solvents are acetone, 2-butanone, benzene, diethyl ether, etc. The reaction usually proceeds without the need for external heating and is generally effected at or below room temperature.

The N,N-disubstituted aminomethylcarboxylic acid may be incorporated into the silver halide emulsion of a photographic element or in a layer contiguous to the silver halide emulsion in any amount which will stabilize the silver halide emulsion against fog. In general, a concentration of the N,N-disubstituted aminomethylcarboxylic acid in an amount of from about 0.01 to about 10, preferably about 0.015 to about 0.5 gram per mole of silver in the silver halide emulsion can be used with good results.

The preparation of photographic silver halide emulsions such as are suitably stabilized with an N,N-disubstituted aminomethylcarboxylic acid typically involves three separate operations: (1) emulsification and digestion of silver halide, (2) the freeing of the emulsion of excess water-soluble salts, suitably by washing with water, and (3) the second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954). The N,N-disubstituted aminomethylcarboxylic acid can be added to the emulsion before the final digestion or after-ripening or it can be added immediately prior to the coating. It may be added as a free acid or as its salts.

The silver halide emulsion of a photographic element containing the antifoggants of this invention can contain conventional addenda such as gelatin plasticizers, coating aids, and hardeners such as aldehyde hardeners, e.g., formaldehyde, mucochloric acid, glutaraldehyde bis-sodium bisulfite), maleic dialdehyde, aziridines, dioxane derivatives and oxypolysaccharides. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls, and hemicyanines. Sensitizing dyes useful in sensitizing such emulsions are described, for example in U.S. Patents 2,526,632 of Brooker and White issued Oct. 24, 1950, and 2,503,776 of Sprague issued Apr. 11, 1950. Developing agents can also be incorporated into the silver halide emulsion if desired or can be contained in a contiguous layer. Various silver salts can be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide. The silver halides used can be those which form latent images predominantly on the surface of the silver halide grains or those which form latent images inside the silver halide crystals such as described in U.S. Patent 2,592,250 of Davey and Knott issued Apr. 8, 1952.

The silver halide emulsion layer of a photographic element containing the antifoggants of the invention can contain any of the hydrophilic, water-permeable binding materials suitable for this purpose. Suitable materials include gelatin, colloidal albumin, polyvinyl compounds, cellulose derivatives, acrylamide polymers, etc. Mixtures of these binding agents can also be used. The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Patents 3,142,568 of Nottorf issued July 28, 1964; 3,193,386 of White issued July 6, 1965; 3,062,674 of Houck, Smith and Yudelson issued Nov. 6, 1962; and 3,220,844 of Houck, Smith and Yudelson issued Nov. 30, 1965; and include the water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The silver halide emulsion of a photographic element



containing the antifoggants of the invention can be coated on a wide variety of supports. Typical supports are cellulose nitrate film, cellulose ester film, polyvinyl acetal film, polystyrene film, poly(ethylene terephthalate) film and related films or resinous materials as well as glass, paper, metal and the like. Supports such as paper which are coated with a α-olefin polymers, particularly polymers or α-olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylene-butene copolymers and the like can also be employed.

The speed of the photographic emulsions containing the antifoggants of the invention can be further enhanced by including in the emulsions a variety of hydrophilic colloids such as carboxymethyl protein of the type described in U.S. Patent 3,011,890 of Gates, Jr., Miller and Koller issued Dec. 5, 1961, and polysaccharides of the type described in Canadian Patent 635,206 of Koller and Russell issued Jan. 23, 1962.

Photographic emulsions containing the antifoggants of the invention can also contain speed-increasing compounds such as quaternary ammonium compounds, polyethylene glycol or thioethers. Frequently, useful effects can be obtained by adding the afore-mentioned speed-increasing compounds to the photographic developer solutions instead of, or in addition to, the photographic emulsions.

Photographic elements containing the antifoggants of the instant invention can be used in various kinds of photographic systems. In addition to being useful in X-ray and other non-optically sensitized systems, they can also be used in orthochromatic, panchromatic and infrared sensitive systems. The sensitizing addenda can be added to photographic systems before or after any sensitizing dyes which are used.

Silver halide emulsions containing the antifoggants of the invention can be used in color photography, for example, emulsions containing color forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type such as described in U.S. Patent 2,698,794 of Godowsky issued Jan. 4, 1955; in silver dye-bleach systems; and emulsions of the mixed-grain type such as described in U.S. Patent 2,592,243 of Carroll and Hanson issued Apr. 8, 1952.

Silver halide emulsions containing the antifoggants of the invention can be sensitized using any of the well-known techniques in emulsion making, for example, by digesting with naturally active gelatin or various sulfur, selenium, tellurium compounds and/or gold compounds. The emulsions can also be sensitized with salts of noble metals of Group VIII of the Periodic Table which have an atomic weight greater than 100.

Silver halide emulsions containing the antifoggants of the invention can be used in diffusion transfer processes which utilize the undeveloped silver halide in non-image areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a silver layer in close proximity to the original silver halide emulsion layer. Such processes are described in U.S. Patents 2,352,014 of Rott issued June 20, 1944; 2,543,181 of Land issued Feb. 27, 1951; and 3,020,155 of Yackel, Yutzy, Foster and Rasch issued Feb. 6, 1962. The emulsions can also be used in diffusion transfer color processes which utilize a diffusion transfer of an imagewise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Silver halide emulsions containing the antifoggants of the invention can be processed in stabilization processes such as the ones described in U.S. Patent 2,614,927 of Broughton and Woodward issued Oct. 21, 1952, and as described in the article "Stabilization Processing of Films and Papers" by H. D. Russell, E. C. Yackel and J. S. Bruce in P.S.A. Journal, Photographic Science and Technique, Volume 16B, October 1950.

While it is preferred to utilize the antifoggants of the invention by incorporating them directly into a photographic element, the antifoggants could also be utilized by incorporating them into a photographic developer to control development fog.

The antifogging agents of this invention can be incorporated to advantage during manufacture in silver halide emulsions representing the variations described above. Moreover, fog control in binderless silver halide films prepared by vapor deposition of silver halide on a suitable support can be achieved by coating the antifogging agents of the invention over the vapor deposited layer of silver halide.

Combinations of all the above-mentioned addenda can be used if desired.

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

## EXAMPLE 1

Preparation of 2-(piperidinomethylthio)succinic acid

To a cooled solution of 75 g. (0.5 mole) of mercaptosuccinic acid in 250 ml. of acetone is added slowly 85.5 g. (0.5 mole) of isobutoxymethylpiperidine. The white solid which separates is collected on a filter, washed with acetone and dried under vacuum. Yield, 75 g. (60 percent), M.P. 160 to 161° C.

*Analysis.*—Calc'd (percent): C, 48.7; H, 7.0; N, 5.7; S, 13.0. Found (percent): C, 48.5; H, 6.7; N, 5.4; S, 13.1.

## EXAMPLES 2 TO 6

The process described in Example 1 is repeated except that amines having the formulae

$$\underset{R_1}{\overset{R}{N}}-CH_2O-CH_2-\overset{CH_3}{CH}-CH_3$$

wherein the groups

$$\underset{R_1}{\overset{R}{N}}-$$

are defined in Table 1, are substituted for isobutoxymethylpiperidine. The resultant products have the formulae

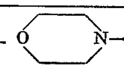
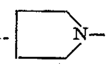
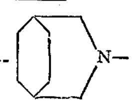
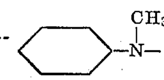
$$\underset{R_1}{\overset{R}{N}}-CH_2S\overset{COOH}{CH}CH_2COOH$$

wherein the groups

$$\underset{R_1}{\overset{R}{N}}-$$

are defined in Table 1. The properties of these products are given in Table 1.

TABLE 1

| Example | $R(R_1)N-$ | M.P., ° C. | Calculated C | Calculated H | Calculated N | Calculated S | Found C | Found H | Found N | Found S |
|---|---|---|---|---|---|---|---|---|---|---|
| 2 |  | 174–75 | 43.3 | 6.1 | 5.6 | 12.8 | 43.2 | 6.1 | 5.6 | 12.6 |
| 3 |  | 121–26 | 46.4 | 6.5 | 6.3 | 13.7 | 46.9 | 6.4 | 6.0 | 13.9 |
| 4 |  | 140–42 | 54.4 | 7.4 | 4.9 | 11.2 | 53.7 | 7.2 | 4.6 | 11.3 |
| 5 |  | 90–93 | 52.3 | 7.7 | 5.1 | 11.6 | 52.2 | 7.6 | 4.7 | 11.3 |
| 6 | $(C_2H_5)_2N-$ | 45–50 | 45.9 | 7.3 | 6.0 | 13.6 | 44.9 | 7.2 | 5.4 | 12.4 |

(Analysis (percent))



## EXAMPLE 7

Preparation of 2-(piperidinomethylthio)propionic acid

To a cooled solution of 10.6 g. (0.1 mole) of thiolactic acid in 250 ml. of diethyl ether is added slowly 17.1 g. (0.1 mole) of isobutoxymethylpiperidine. The product which separates from the warm reaction mixture is collected on a filter and dried under vacuum. Yield, 18 g. (89 percent), M.P. 86–87° C.

*Analysis.*—Calc'd (percent): C, 53.2; H, 8.4; N, 6.9; S, 15.7. Found (percent): C, 53.5; H, 8.6; N, 6.8; S. 15.4.

## EXAMPLES 8 TO 10

The process described in Example 7 is repeated except that amines having the formulae

$$\underset{R_1}{\overset{R}{N}}-CH_2O-CH_2-\overset{CH_3}{CH}-CH_3$$

wherein the groups

$$\underset{R_1}{\overset{R}{N}}-$$

are defined in Table 2, are substituted for isobutoxymethylpiperidine. The products thus obtained have the formulae

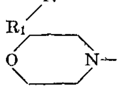
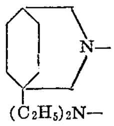
$$\underset{R_1}{\overset{R}{N}}-CH_2S\underset{CH_3}{CH}COOH$$

wherein the groups

$$\underset{R_1}{\overset{R}{N}}-$$

are defined in Table 2. The properties and yields of these products are given in Table 2.

TABLE 2

| Ex. | $R_1(R)N-$ | M.P., ° C. | Percent yield | Analysis (percent) Calculated C | H | N | S | Found C | H | N | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 |  | 80-81 | 78 | 46.8 | 7.4 | 6.8 | 15.6 | 47.0 | 7.6 | 6.5 | 15.5 |
| 9 |  | 139-40 | 87 | 59.3 | 8.7 | 5.8 | 13.2 | 59.1 | 8.3 | 5.7 | 13.2 |
| 10 | $(C_2H_5)_2N-$ | 60-61 | 68 | 50.2 | 9.0 | 7.3 | 16.8 | 50.2 | 9.3 | 7.4 | 16.7 |

## EXAMPLE 11

Preparation of 2-(piperidinomethylthio)acetic acid

To a cooled solution of isobutoxymethylpiperidine (85.5 g., 0.5 mole) in 250 ml. of benzene is added slowly 46.6 g. (0.5 mole) of mercaptoacetic acid. The crystalline product, M.P. 75–76° C., 50 g. (53 percent), which separates on standing at room temperature, is collected on a filter washed with diethyl ether and dried under vacuum.

*Analysis.*—Calc'd (percent): C, 50.7; H, 8.0; N, 7.4; S, 16.9. Found (percent): C, 50.8; H, 8.2; N, 7.4; S, 16.7.

## EXAMPLES 12 to 16

The process described in Example 11 is repeated except that amines having the formulae

$$\underset{R_1}{\overset{R}{N}}-CH_2O-CH_2-\overset{CH_3}{CH}-CH_3,$$

wherein the groups

$$\underset{R_1}{\overset{R}{N}}-$$

are defined in Table 3, are substituted for isobutoxymethylpiperidine. The resultant products have the formulae

$$\underset{R_1}{\overset{R}{N}}-CH_2SCH_2CH_2COOH$$

wherein the groups

$$\underset{R_1}{\overset{R}{N}}-$$

are defined in Table 3. The yields and properties of these products are given in Table 3.

## EXAMPLE 17

Preparation of 3-(piperidinomethylthio)propionic acid

To a cooled solution of 21.2 g. (0.2 mole) of 3-mercaptopropionic acid in 150 ml. of benzene is added 34.2 g. (0.2 mole) of isobutoxymethylpiperidine. The benzene-isobutanol azeotrope is removed by distillation, and the liquid residue is dried on a rotary vacuum dryer. Further purification of the clear liquid product (M.P. 0.1° C.) is not carried out.

*Analysis.*—Calc'd. (percent): C, 53.2. H, 8.5. , 6.9. Found (percent): C, 53.4; H, 8.9; N, 6.2.

## EXAMPLES 18 to 21

The process described in Example 17 is repeated except that amines having the formulae

$$\underset{R_1}{\overset{R}{N}}-CH_2O-CH-\overset{CH_3}{CH}-CH_2$$

wherein the groups

$$\underset{R_1}{\overset{R}{N}}-$$

are defined in Table 4, are substituted for isobutoxymethylpiperidine. The products thus obtained have the formulae

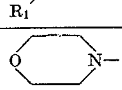
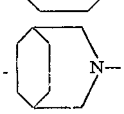
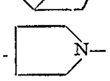
$$\underset{R^1}{\overset{R}{N}}-CH_2SCH_2CH_2COOH$$

wherein the groups

$$\underset{R_1}{\overset{R}{N}}-$$

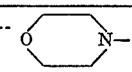
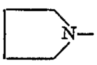
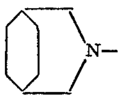
are defined in Table 4. The properties of these products are given in Table 4.

TABLE 3

| Ex. | $R_1(R)N-$ | M.P., ° C. | Percent yield | Analysis (percent) Calculated C | H | N | S | Found C | H | N | S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 |  | 95-96 | 79 | 43.9 | 6.9 | 7.3 | 16.8 | 43.7 | 6.8 | 7.1 | 16.6 |
| 13 |  | 153-54 | 44 | 57.5 | 8.3 | 6.1 | 13.9 | 57.8 | 8.3 | 5.8 | 13.8 |
| 14 |  | (1) | 70 | 47.9 | 7.5 | 8.0 | 18.3 | 47.1 | 7.3 | ...... | 18.0 |
| 15 | $(C_2H_5)_2N-$ | 50-51 | 68 | 47.4 | 8.5 | 7.9 | 18.1 | 48.3 | 8.2 | 7.5 | 18.5 |
| 16 | $(C_8H_{17})_2N-$ | (2) | ......... | 66.2 | 11.4 | ...... | ...... | 66.0 | 10.6 | ...... | ...... |

1 Waxy, solid.
2 Yellow oil.

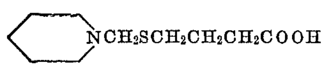
TABLE 4

| Example | R(R₁)N— | M.P., °C. | Calculated C | Calculated H | Calculated N | Found C | Found H | Found N |
|---|---|---|---|---|---|---|---|---|
| 18 |  | 84-85 | 47.7 | 7.4 | 6.8 | 45.7 | 7.3 | 6.7 |
| 19 |  | 0.1 | 50.6 | 8.0 | 7.4 | 53.5 | 9.1 | 7.3 |
| 20 |  | 0.1 | 59.3 | 8.7 | ------ | 58.1 | 8.4 | ------ |
| 21 | $(C_2H_5)_2N-$ | 0.1 | ------ | ------ | ------ | ------ | ------ | ------ |

## EXAMPLE 22

Preparation of 4-(piperidinomethylthio)butyric acid

Isobutoxymethylpiperidine (17.1 g., 0.1 mole) and 4-mercaptobutyric acid (12.0 g., 0.1 mole) are reacted, with cooling. The product is washed with ligroin and dried under vacuum. The resulting yellow oil ($n_D^{25}$ 1.4860) is not purified further. The product has the structural formula



## EXAMPLE 25

Preparation of 2-morpholinomethylmercapto-3-phenylacrylic acid

A mixture of 10.0 g. (0.06 mole) of isobutoxymethylmorpholine and 9.0 g. (0.05 mole) of 3-phenyl-2-mercaptoacrylic acid are warmed gently on a hot plate until solution is complete. The resulting solution is cooled and triturated with diethyl ether to produce 6.0 g. (46 percent) of a yellow solid, M.P. indeterminate (with decomposition over a broad range).

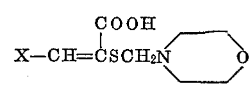
*Analysis.*—Calc'd (percent): C, 60.2; H, 6.0; N, 5.0; S, 11.4. Found (percent): C, 60.1; H, 6.5; N, 5.4; S, 11.0.

## EXAMPLES 26 to 29

The process described in Example 25 is repeated except that an acid having the formula

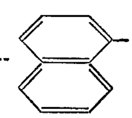
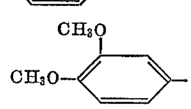
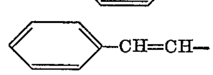
$$X-CH=\underset{\displaystyle SH}{\underset{|}{C}}-COOH$$

wherein the groups X are defined in Table 6, are substituted for the 3-phenyl-2-mercaptoacrylic acid. The resultant products have the formulae



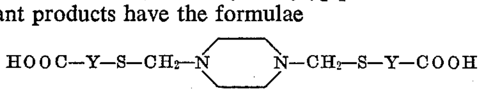
wherein the groups X are defined in Table 6. The analyses of these products are given in Table 6. The melting points of the products are over a wide range above 75–80° C. with decomposition.

TABLE 6

| Example | X | Calculated C | Calculated H | Calculated N | Calculated S | Found C | Found H | Found N | Found S |
|---|---|---|---|---|---|---|---|---|---|
| 26 |  | 53.4 | 5.6 | 5.2 | 11.8 | 54.7 | 5.4 | 5.5 | 9.3 |
| 27 |  | 65.7 | 5.8 | 4.2 | ------ | 64.2 | 6.3 | 5.4 | ------ |
| 28 |  | 65.5 | 6.3 | 4.1 | 9.4 | 56.5 | 6.5 | 4.9 | 8.6 |
| 29 |  | 62.9 | 6.3 | 4.6 | 10.4 | 62.7 | 6.4 | 5.0 | 10.0 |

## EXAMPLES 23 and 24

The process of Examples 7 and 11 are repeated except that the isobutoxymethylpiperidine in each example is replaced with di(isobutoxymethyl)piperazine. The resultant products have the formulae



wherein the groups Y are defined in Table 5. The yields and properties of these products are given in Table 5.

TABLE 5

| Example | Y | M.P., °C. | Percent yield | Calculated C | Calculated H | Calculated N | Calculated S | Found C | Found H | Found N | Found S |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 23 | $-CH(CH_3)-$ | 164-65 | 94 | 44.7 | 7.1 | 8.7 | 19.9 | 44.7 | 7.0 | 8.5 | 20.0 |
| 24 | $-CH_2-$ | 173-75 | 88 | 40.8 | 6.2 | 9.5 | 20.9 | 40.5 | 6.2 | 9.4 | 21.0 |

Each of the compounds prepared in Examples 1 to 29 are added to separate portions of a high speed silver bromoiodide emulsion. Each emulsion sample is coated on a cellulose acetate film support at a coverage of 459 mg. of silver and 1040 mg. of gelatin per square foot. A sample of each film coating is exposed on an intensity scale sensitometer, processed for five minutes in Kodak Developer DK–50, fixed, washed and dried. The photographic results obtained from these tests are listed in Table 7.

TABLE 7

| Compound prepared in example | Conc. of compound in g./mole Ag | Fresh: Rel. speed | Fresh: Gamma | Fresh: Fog | 2 week incubation at 120° F. and 50% relative humidity: Rel. speed | 2 week incubation at 120° F. and 50% relative humidity: Gamma | 2 week incubation at 120° F. and 50% relative humidity: For |
|---|---|---|---|---|---|---|---|
| Control |  | 100 | 1.23 | 0.17 | 26 | 0.57 | 0.99 |
| 22 | 0.03 | 52 | 0.97 | 0.13 | 36 | 0.87 | 0.21 |
| 16 | 0.03 | 35.5 | 0.92 | 0.11 | 28 | 0.85 | 0.16 |
| Control |  | 100 | 1.23 | 0.09 | 27.5 | 0.72 | 0.81 |
| 17 | 0.03 | 97 | 1.22 | 0.09 | 43 | 0.90 | 0.34 |
| 18 | 0.03 | 85 | 1.18 | 0.08 | 54 | 1.07 | 0.45 |
| 19 | 0.03 | 91 | 1.13 | 0.09 | 38 | 0.83 | 0.35 |
| 21 | 0.03 | 89 | 1.12 | 0.09 | 39 | 0.90 | 0.35 |
| 11 | 0.03 | 68 | 1.20 | 0.07 | 71 | 1.05 | 0.13 |
| 12 | 0.03 | 73 | 1.27 | 0.07 | 76 | 1.10 | 0.15 |
| 14 | 0.03 | 83 | 1.33 | 0.06 | 62 | 0.98 | 0.17 |
| 24 | 0.03 | 85 | 1.28 | 0.07 | 74 | 1.00 | 0.18 |
| 1 | 0.03 | 95 | 1.27 | 0.10 | 76 | 1.12 | 0.29 |
| 2 | 0.03 | 97 | 1.18 | 0.07 | 78 | 1.07 | 0.29 |
| 3 | 0.03 | 107 | 1.28 | 0.08 | 53 | 0.93 | 0.32 |
| 5 | 0.3 | 59 | 1.12 | 0.06 | 43 | 0.98 | 0.07 |
| 6 | 0.3 | 63 | 1.25 | 0.06 | 53 | 1.17 | 0.07 |
| Control |  | 100 | 1.37 | 0.12 | 21 | 0.77 | 0.98 |
| 20 | 0.15 | 52 | 1.00 | 0.10 | 20.5 | 0.88 | 0.37 |
| 13 | 0.03 | 87 | 1.22 | 0.10 | 36 | 0.72 | 0.70 |
| 4 | 0.03 | 89 | 1.15 | 0.14 | 25 | 0.68 | 0.74 |
| Control |  | 100 | 1.32 | 0.12 | 20 | 0.70 | 0.97 |
| 7 | 0.045 | 68 | 1.13 | 0.08 | 53 | 0.97 | 0.18 |
| 8 | 0.03 | 76 | 1.15 | 0.09 | 45 | 0.93 | 0.31 |
| 23 | 0.045 | 57 | 1.00 | 0.07 | 47 | 0.85 | 0.17 |
| Control |  | 100 | 1.23 | 0.12 | 28 | 0.75 | 0.83 |
| 9 | 0.06 | 69 | 1.15 | 0.08 | 63 | 0.97 | 0.11 |
| 15 | 0.06 | 55 | 1.13 | 0.08 | 49 | 0.93 | 0.12 |
| Control |  | 100 | 1.10 | 0.11 | 44 | 0.95 | 0.91 |
| 10 | 0.03 | 91 | 1.22 | 0.10 | 76 | 1.17 | 0.26 |
| Control |  | 100 | 1.25 | 0.11 | 48 | 0.97 | 0.62 |
| 25 | 0.15 | 87 | 1.13 | 0.20 | 50 | 0.90 | 0.55 |
| Control |  | 100 | 1.20 | 0.11 | 37 | 0.82 | 0.55 |
| 26 | 0.15 | 85 | 1.10 | 0.20 | 29.5 | 0.88 | 0.50 |
| 27 | 0.15 | 78 | 1.07 | 0.24 | 33 | 0.88 | 0.51 |
| 28 | 0.15 | 85 | 1.10 | 0.18 | 40 | 0.88 | 0.44 |
| 29 | 0.15 | -------- | 0.97 | ------ | 22 | 0.82 | 0.55 |

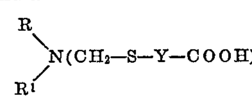
The results in the above table show that the compounds of the invention prevent the growth of incubation fog when incorporated in photographic emulsions.

Although the invention has been described in considerable detail with reference to certain embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove and as defined in the appended claims. For example, esters and salts, such as hydrochloride salts, and other derivatives of the N,N-disubstituted aminomethylthiocarboxylic acids may be prepared by known techniques and used in the same manner as the acids.

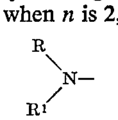
We claim:

**1.** A composition comprising a photographic silver halide emulsion containing a fog-stabilizing amount of an N,N-disubstituted aminomethylthiocarboxylic acid.

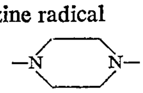
**2.** A composition comprising a photographic silver halide emulsion containing a fog-stabilizing amount of an N,N-disubstituted aminomethylthiocarboxylic acid having the general formula



wherein $n$ is either 1 or 2, and, when $n$ is 1, R and $R^1$ are members selected from the group consisting of alkyl, cycloalkyl, aryl and aralkyl and, when taken together with the nitrogen atom to which they are attached comprise a primary heterocyclic ring containing from 5 to 7 atoms in the ring, and, when $n$ is 2, the group



is the divalent piperazine radical

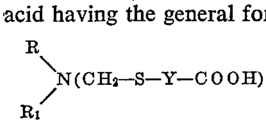


and wherein Y is selected from the group consisting of alkylene groups and alkyl, aryl, carboxy or carboxyalkyl substituted alkylene groups.

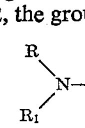
**3.** The composition of claim **2** wherein said N,N-disubstituted aminomethylthiocarboxylic acid is present in an amount of from about 0.01 to about 10 grams per mole of silver in said silver halide emulsion.

**4.** A photographic element comprising a support coated with a silver halide layer, said element containing a fog-stabilizing amount of an N,N-disubstituted aminomethylthiocarboxylic acid.

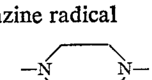
**5.** A photographic element comprising a support coated with a silver halide layer, said element containing a fog-stabilizing amount of an N,N-disubstituted aminomethylthiocarboxylic acid having the general formula



wherein $n$ is either 1 or 2, and, when $n$ is 1, R and $R^1$ are members selected from the group consisting of alkyl, cycloalkyl, aryl and aralkyl and, when taken together with the nitrogen atom to which they are attached comprise a primary heterocyclic ring containing from 5 to 7 atoms in the ring, and when $n$ is 2, the group



is the divalent piperazine radical



and wherein Y is selected from the group consisting of alkylene groups and alkyl, aryl, carboxy or carboxyalkyl substituted alkylene groups.

**6.** The photographic element of claim **5** wherein said layer is a silver halide emulsion.

**7.** The photographic element of claim **5** wherein said aminomethylthiocarboxylic acid is present in an amount of from about 0.01 to about 10 grams per mole of silver in said silver halide emulsion.

**8.** The photographic element of claim **5** wherein said N,N-disubstituted aminomethylthiocarboxylic acid is present in said silver halide emulsion.

**9.** The photographic element of claim **5** wherein said N,N-disubstituted aminomethylthiocarboxylic acid is present in a layer contiguous to said silver halide emulsion.

**10.** In the process of developing a photographic element comprising a support coated with at least one silver halide emulsion layer, the improvement comprising developing said photographic element in the presence of an N,N-disubstituted aminomethylthiocarboxylic acid.

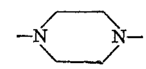
**11.** In a process of developing a photographic element comprising a support coated with at least one silver halide emulsion layer, the improvement comprising developing said photographic element in the presence of an N,N-disubstituted aminomethylthiocarboxylic acid having the general formula

$$\begin{matrix} R \\ & \searrow \\ & & N(CH_2-S-Y-COOH)_n \\ & \nearrow \\ R_1 \end{matrix}$$

wherein *n* is either 1 or 2, and, when *n* is 1, R and R[1] are members selected from the group consisting of alkyl, cycloalkyl, aryl and aralkyl and, when taken together with the nitrogen atom to which they are attached comprise a primary heterocyclic ring containing from 5 to 7 atoms in the ring, and, when *n* is 2, the group

$$\begin{matrix} R \\ & \searrow \\ & & N- \\ & \nearrow \\ R_1 \end{matrix}$$

is the divalent piperazine radical



and wherein Y is selected from the group consisting of alkylene groups and alkyl, aryl, carboxy or carboxyalkyl substituted alkylene groups.

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NORMAN G. TORCHIN, Primary Examiner

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U.S. Cl. X.R.

96—109; 260—471