

[54] **INCORPORATION OF SULFONYL  
DERIVATIVES OF ISOTHIIOUREA IN  
LIGHT-SENSITIVE ELEMENTS**

[75] Inventors: **Donald M. Burness; Grant M. Haist,**  
both of Rochester; **James R. King,**  
Webster, all of N.Y.

[73] Assignee: **Eastman Kodak Company,**  
Rochester, N.Y.

[22] Filed: **Apr. 2, 1973**

[21] Appl. No.: **347,314**

[52] U.S. Cl. .... **96/61 R, 96/66 T, 96/76 R,**  
96/95

[51] Int. Cl. .... **G03c 5/38, G03c 1/48, G03c 1/06**

[58] Field of Search ..... **96/61 R, 76 R, 109, 66 R,**  
96/66 T

|      |                              |        |                   |         |
|------|------------------------------|--------|-------------------|---------|
| [56] | <b>References Cited</b>      |        |                   |         |
|      | <b>UNITED STATES PATENTS</b> |        |                   |         |
|      | 3,140,178                    | 7/1964 | Herz et al. ....  | 96/61 R |
|      | 3,189,453                    | 6/1965 | Herz et al. ....  | 96/61 R |
|      | 3,506,444                    | 4/1970 | Haist et al. .... | 96/61 R |
|      | T887,024                     | 6/1971 | Haist .....       | 96/61 R |

*Primary Examiner*—Mary F. Kelley  
*Attorney, Agent, or Firm*—Henry E. Byers

[57] **ABSTRACT**

Sulfonylalkyl or sulfonamidoalkyl isothiuronium compounds, incorporated in emulsions containing silver salts and processing chemicals, can be activated by immersion, heat or ammonia gas to form light-stable photographic images.

**22 Claims, No Drawings**

# INCORPORATION OF SULFONYL DERIVATIVES OF ISOTHIUREA IN LIGHT-SENSITIVE ELEMENTS

## BACKGROUND OF THE INVENTION

This invention relates to photographic elements having incorporated sulfonylalkyl and sulfonamidoalkyl isothiuronium compounds and methods of employing these compounds for stabilizing photographic images.

U.S. Pat. No. 3,506,444, issued Apr. 14, 1970 to Haist et al., describes the use of isothiurea derivatives containing a sulfonate radical for the dry stabilization of silver halide photographic emulsions at a temperature of above about 90°C. These isothiurea derivatives function as precursors for image stabilizers in photographic elements. They are stable and substantially inert when incorporated in silver halide emulsions or in layers contiguous to such silver halide emulsions at temperatures which ordinarily prevail during conventional storage and use of photographic products. At the elevated temperatures of above about 90°C, preferably above about 150°C, the isothiurea derivatives are converted to thiol compounds which form light stable mercaptides with the silver halide in the unexposed areas of the photographic emulsion.

In heat processing of silver halide emulsions containing an incorporated stabilizer precursor, the rate of processing is a function of heat and time. For instance, a temperature of 190°C might produce a satisfactory density in 2 seconds. A shorter time would be required for a higher temperature, provided, of course, that the temperature would not reach decomposition temperatures. However, in view of the difficulty in providing satisfactorily high temperatures for a given period of time for processing exposed photographic elements, it has been desirable to find stabilization precursors which could be used which would permit processing at a lower temperature without increasing the processing time.

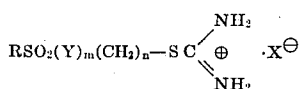
Accordingly, it is an object of the invention to provide a new class of stabilizer precursors that can be incorporated directly in the emulsion layers of light-sensitive photographic materials which can be used at a lower temperature than prior art stabilizers without increasing processing time. Another object of the invention is to provide stabilizer precursors that are in an unreactive form at the pH of the coating composition but are converted to an active form easily by alkaline treatment or by heating.

A further object is to provide certain stabilizer precursors which are more readily cleaved to release stabilizers than known incorporated blocked silver stabilizing precursors so that heat activated systems may be designed to produce image stabilization at lower temperatures of activation than in prior art systems.

## SUMMARY OF THE INVENTION

The above objects are attained by using stabilizer precursors of this invention which are sulfonylalkyl or sulfonamidoalkyl isothiuronium compounds.

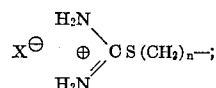
In one embodiment, the isothiuronium compounds have the formula:



wherein:

$m = 0$  or  $1$ ;

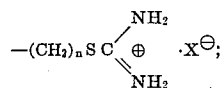
$R$  = alkyl having 1-5 carbon atoms, aryl having 6-12 carbon atoms or



$Y = \text{NR}'$  or  $\text{ZSO}_2$ ;

$Z$  = divalent hydrocarbon radical having 1-5 carbon atoms or a carbon chain containing  $-\text{C}-\text{O}-\text{C}-$ ;

$R' = \text{H}$ , alkyl having 1-5 carbon atoms or



$n = 2$  or  $3$  and

$\text{X}^-$  is a non-metallic acid anion.

Non-metallic acid anions can be any suitable anion. Particularly suitable anions include halide such as; for example, chloride, bromide, iodide, tosylate, mesylate, sulfate, nitrate, acetate, trifluoroacetate, benzoate, etc.

According to the present invention, an exposed photographic silver halide may be stabilized by a process wherein a sulfonylalkyl or sulfonamidoalkyl isothiuronium compound is incorporated in a photographic silver halide element.

One embodiment of the invention comprises a substantially dry stabilization method which comprises heating an exposed photographic silver halide element comprising a silver halide emulsion in the presence of an active stabilizing amount of sulfonylalkyl or sulfonamidoalkyl isothiuronium compound at a temperature above about 90°C to about 260°C.

The above sulfur-containing compounds function as precursors for image stabilizers in the present process and are stable and substantially inert in silver halide emulsions or in layers contiguous to such silver halide emulsions at temperatures which ordinarily prevail during the conventional storage and use of photographic products. At the elevated temperatures set out above, the sulfur-containing compounds of the invention are converted to thiol compounds which form light-stable mercaptides with the silver halide in the unexposed areas of the photographic emulsion.

## PREFERRED EMBODIMENTS

The isothiurea derivatives are utilized in the present process typically at concentrations of at least  $\frac{1}{4}$  to about 20 moles for each mole of silver halide. However, it is preferable to utilize molar excesses of the isothiuronium compound to assure effective stabilization of the unexposed and undeveloped areas of the silver halide emulsion. In order to prevent printout and other adverse effects, such as image obliteration, commonly at least 5 or in certain instances, even 10 times as much of the isothiuronium compound can be utilized than is

required on a molar basis to stabilize the silver halide in the emulsion.

Small amounts of moisture, amounts of the order present in the conventional photographic paper supports under typical room conditions, such as 25°C and 40 percent relative humidity, are catalytic to the heat cleaving action which takes place in the process of the invention and can be useful in the process of stabilizing. Such small amounts of water can be residual water from prior processing steps, which may be found desirable. Such moisture may be made available essentially during the heating step of the present process. It has been found that certain hygroscopic materials, such as sodium sulfate and the like, when combined with the photographic elements treated by the process of the invention can be useful.

The isothiuronium compounds used in the process of the invention can be employed with various kinds of photographic emulsions. Suitable emulsions which are useful include orthochromatic, panchromatic, infra-red emulsions, as well as X-ray films and other non-optically sensitized emulsions. Various silver salts may be employed in such emulsions as the sensitive salts. These include such salts as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide, silver bromiodide, or silver chloriodide.

Typically, the emulsion containing such salts has these salts dispersed or suspended in gelatin or other suitable permeable vehicles such as polyvinyl alcohol, polyacrylates, acrylic acids or other permeable polymers. Other permeable materials which may be used include colloidal albumin and cellulose derivatives. Suitable binding agents may be employed with the photographic elements of the invention such as cellulose acetates and cellulose ethers.

The emulsion utilized in preparing the photographic elements can be coated on a wide variety of supports. Typical suitable photographic supports are cellulose ester film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film and related films or resinous materials. Suitable supports such as glass, paper, wood, metals and others employed in the photographic art can be used. It is desirable to employ a support which is resistant to decomposition or other adverse effects on the photographic element at the temperatures employed in the process. It is, accordingly, desirable to employ a support resistant to charring at elevated temperatures.

The silver halide elements processed according to the invention may be sensitized using any of the well-known techniques in emulsion making. For example, they may be prepared by digesting with naturally active gelatin or various sulfur, selenium, tellurium or gold compounds. They may also be sensitized with salts of noble metals and may also contain speed-increasing addenda such as quaternary ammonium salts, polyethylene glycols or other suitable sensitizers. The emulsions treated according to the invention may also contain conventional addenda or have such addenda in layers contiguous to the emulsion layers. These addenda include suitable anti-foggants, plasticizers, toners, coating aids, development restrainers, buffers and hardeners. Sensitizing dyes may also be employed as well as spectral sensitizers.

It is often desirable to incorporate a matting agent such as silica with or contiguous to the emulsion.

The isothiuronium compounds can be added to or incorporated in photographic emulsions or layers of photographic elements by using any of the photographic techniques used in emulsion making. For example, they may be dissolved in a suitable solvent and added as such, or they can be added in the form of a dispersion similar to the techniques used to incorporate certain types of color-forming compounds, such as couplers, in a photographic emulsion. Techniques of this type are disclosed in, for instance, U.S. Pat. No. 2,322,027, Jelley et al, and U.S. Pat. No. 2,801,171, Fierke et al. Solvents or diluents which are miscible with water may be utilized to aid in the addition also. Such solvents should be selected in order to avoid adverse effects upon the emulsion or processing steps according to the invention.

In carrying out the process of the invention, the photographic elements described can be exposed and developed by dry or solution methods. Thereafter they can be fixed or stabilized in accordance with the invention by heating to an elevated temperature. It is also often suitable to incorporate a developing agent into the emulsion or a layer contiguous thereto whereby development and stabilization may be effected, without separate steps, upon heating to the desired temperature.

Development can be effected with conventional developers including phenolic developing agents such as hydroquinone, halogen-substituted hydroquinone developers such as chlorohydroquinone, bromohydroquinone, and dichlorohydroquinone, as well as other suitable hydroquinone compounds such as alkyl-substituted hydroquinones. Amino phenol developers such as N-methyl-p-amino-phenol sulfate can also be employed. 3-pyrazolidone developers as, for example, 1-phenyl-3-pyrazolidone, 4-methyl-4-hydroxy-methyl-1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-2-acetyl-4-methyl-3-pyrazolidones such as disclosed in British Pat. No. 930,572 or other related developers are also suitable. Mixtures of developers are especially suitable including, for example, mixtures of hydroquinone developers with 3-pyrazolidone developers.

The developer can be applied in a thin layer over the exposed photographic element, for example, and undeveloped and unexposed silver halide thereafter light-stabilized or fixed by bringing the photographic element in contact with a heating means such as a heated roller or plate.

It is usually desirable to incorporate an activator such as an organic activator precursor with the photographic silver halide emulsion in the process of the invention. Activator as employed herein is intended to refer to an agent which causes the isothiuronium compound to form a compound which combines with the unexposed silver halide of a photographic silver halide emulsion. Inorganic alkalies which may be employed as activators include potassium and/or sodium carbonates, and potassium and/or sodium hydroxides.

The amount of alkali to be used will be influenced by the solubility and activity of the alkali. Ordinarily, however, about one-fourth mole of alkali per mole of silver present in the emulsion as silver halide up to about 20 moles of alkali per mole of silver is suitable. Typically about one-half mole of alkali per mole of silver present in the emulsion as silver halide up to about 10 moles of alkali per mole of silver can be employed.

Since the isothiuronium compounds can be activated by these alkalis, it is usually desirable not to contact the isothiuronium compounds according to the process of the invention with such alkalis until stabilization is desired. For example, in most instances, it would not be desirable to contact a silver halide emulsion with an alkaline aqueous solution of a developer since it would be possible that the stabilization effect caused by the precursors of the invention would take place before the desired degree of development.

It is usually desirable to employ an organic activator precursor incorporated in a silver halide emulsion or in a layer contiguous to the silver halide emulsion according to the present process. Such activator precursors break down or cleave when treated at the elevated temperatures set out above forming compounds which cause the isothiuronium compounds, according to the process, in turn to break down.

Organic activator precursor, as employed herein, is intended to refer to organic compounds which upon heating form moieties which cause or aid in causing cleavage or break down of the described isothiuronium compounds. Suitable activator precursors are typically those which upon heating form an alkaline component. These include, for example, quaternary ammonium activator precursors such as guanidinium organic acid salts, including guanidinium trichloroacetate; tetraalkyl ammonium trichloroacetates, such as tetraethyl ammonium trichloroacetate; quaternary ammonium malonates, such as piperazinium malonate; amino acids, such as aminobutyric acid and aminocaproic acid; hydrazide compounds, such as benzhydrazide and isonicotinic acid hydrazide. Suitable activator precursors are set out, for example in British Pat. No. 930,572 and U.S. Pat. No. 3,506,444, issued Apr. 14, 1970.

The thiuronium salts of this invention are prepared, for the most part, by modifications of known methods. In the formation of the compounds by direct alkylation of thiourea with the appropriate sulfonyl containing halide or mesylate or tosylate ester, it is found advantageous to use a non-protonic polar solvent such as sulfolane, either alone or admixed with ethanol.

In the event that direct formation of the isothiuronium salts is not possible, as in the case of certain trifluoroacetate or perchlorate salts, a preformed halide or other salt is converted by anion interchange to the desired compound. To prepare certain sulfonylalkyl isothiuronium salts, the corresponding sulfido salts are first made, and these are then oxidized to the desired sulfonyl compound. Useful compounds are not limited to but include those listed in Table I.

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

#### EXAMPLE 1

##### Heat Processing of Incorporated Sulfonyl Isothiuronium Compound

Preparation of 2,2'-Sulfonylbis(ethylisothiuronium chloride);

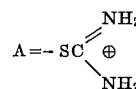
A mixture of 9.55 g (0.05 mole) of bis(2-chloroethyl) sulfone and 7.6 g (0.1 mole) of thiourea are refluxed overnight in a mixture of 125 ml of tetrahydrofuran and 20 ml of tetramethylene sulfone. The reaction mixture is cooled and the resulting crystals collected on a suction funnel. Product melting at

211°-212°C is obtained on recrystallization from a mixture of tetrahydrofuran and methanol.

Analysis calculated for:  $C_{16}H_{16}Cl_2N_4O_2S_3$   
C, 21.0; H, 4.7; N, 16.3; S, 28.0  
Found: C, 21.2; H, 4.5; N, 16.3; S, 27.7.

TABLE I

Isothiuronium salts



Structure

|                                                                  |                  |
|------------------------------------------------------------------|------------------|
| $CH_3SO_2CH_2CH_2A$                                              | $Cl^-$           |
| $CH_3SO_2CH_2CH_2A$                                              | $CF_3CO_2^-$     |
| $CH_3SO_2CH_2CH_2A$                                              | $C_7H_7SO_3^-$   |
| $CH_3SO_2(CH_2)_3A$                                              | $Cl^-$           |
| $CH_3SO_2(CH_2)_3A$                                              | $CF_3CO_2^-$     |
| $O_2S(CH_2CH_2A)_2$                                              | $2 Cl^-$         |
| $O_2S(CH_2CH_2A)_2$                                              | $2 C_7H_7SO_3^-$ |
| $O_2S(CH_2CH_2A)_2$                                              | $2 CF_3CO_2^-$   |
| $O_2S(CH_2CH_2A)_2$                                              | $2 CH_3SO_3^-$   |
| $CH_2(SO_2CH_2CH_2A)_2$                                          | $2 Cl^-$         |
| $CH_2(SO_2CH_2CH_2A)_2$                                          | $2 C_7H_7SO_3^-$ |
| $CH_2(SO_2CH_2CH_2A)_2$                                          | $2 CF_3CO_2^-$   |
| $O(CH_2SO_2CH_2CH_2A)_2$                                         | $2 Cl^-$         |
| $O(CH_2SO_2CH_2CH_2A)_2$                                         | $2 C_7H_7SO_3^-$ |
| $\left[CH_2OCH_2CH_2SO_2CH_2CH_2A\right]_2$                      | $2 CH_3SO_3^-$   |
| $HOCH_2CH_2SO_2CH_2CH_2A$                                        | $C_7H_7SO_3^-$   |
| $CH_3-\text{C}_6\text{H}_4-\text{SO}_2\text{NHCH}_2\text{CH}_2A$ | $C_7H_7SO_3^-$   |
| $CH_3SO_2N(CH_2CH_2A)_2$                                         | $2 Cl^-$         |
| $CH_3SO_2N(CH_2CH_2A)_2$                                         | $2 C_7H_7SO_3^-$ |
| $CH_3SO_2N(CH_2CH_2A)_2$                                         | $2 CH_3SO_3^-$   |
| $CH_3-\text{C}_6\text{H}_4-\text{SO}_2N(CH_2CH_2A)_2$            | $2 C_7H_7SO_3^-$ |
| $CH_3-\text{C}_6\text{H}_4-\text{CH}_3$<br>$CH_3SO_2NCH_2CH_2A$  | $CH_3SO_3^-$     |

The following composition is coated on gelatin coated paper base at 290 mg/ft<sup>2</sup>:

|                                                                                            |      |    |
|--------------------------------------------------------------------------------------------|------|----|
| Gelatin, pigskin, 12% by wt, aqueous                                                       | 50.0 | g  |
| Alkylphenoxypoly(hydroxypropylene oxide)                                                   |      |    |
| Surfactant, 10% by wt., aqueous                                                            | 1.0  | g  |
| 2,2'-Sulfonylbis(ethylisothiuronium chloride)                                              | 1.0  | g  |
| Associated developer compound of hydroquinone and 1-phenyl-3-pyrazolidone, 1:1             | 2.0  | g  |
| Urea                                                                                       | 2.0  | g  |
| Silver chloride photographic emulsion (124 g of gelatin and one mole of silver in 2.33 kg) | 4.5  | ml |

After exposure, a strip of the coated paper is contacted, emulsion side up, for 15 seconds on a metal platen heated to 140°C. A warm brown image of moderate density is produced with a white background that is stable to the continued exposure to light.

#### EXAMPLE 2

##### Non-Aqueous Coating Compositions With A Sulfonyl Isothiuronium Compound

A non-aqueous coating composition is prepared as

below and coated at a 0.0075-inch wet thickness on baryta-coated paper base.

|                                                                       |      |    |
|-----------------------------------------------------------------------|------|----|
| Cellulose propionate, 15% by wt. in methylene chloride-methanol (1:1) | 25.0 | ml |
| Ethylenedithia- $\alpha,\alpha'$ -dipropionic acid                    | 0.7  | g  |
| 2,2'-Sulfonylbis(ethylisothiuronium chloride)                         | 0.5  | g  |
| Guanidinium trichloroacetate                                          | 1.0  | g  |
| Hydroquinone                                                          | 0.5  | g  |
| 4-Methyl-1-phenyl-3-pyrazolidone                                      | 1.0  | g  |
| Silver nitrate (in 0.67 ml water + 3.33 ml methanol)                  | 0.33 | g  |

After exposure, the back of a strip of the above coating is contacted, emulsion side up, for 10 seconds on a platen heated to 140°C. A moderate density image of purpleblack tone is formed with a white background that is light stable.

A strip of the same exposed coating is treated for 60 seconds in gaseous ammonia. A black-toned image of excellent density is obtained with an off-white background that is stable to further light exposure.

### EXAMPLE 3

#### Incorporation of

#### 2,2'-Methylsulfonyliminobis(ethylisothiuronium p-toluenesulfonate)

Preparation of 2,2'-Methylsulfonyliminobis(ethylisothiuronium p-toluenesulfonate):

##### A. N,N-Bis(2-chloroethyl)methanesulfonamide

Methanesulfonyl chloride, 35.7 g (0.2 mole) is added to a solution of 11.46 g (0.1 mole) of di-(2-chloroethyl) ammonium chloride in 100 ml of pyridine over a period of 5 minutes. The resulting dark brown solution is heated for 1 hour on a steam bath. The hot mixture is poured into 400 ml of water and cooled to 10°C. The tan crystals are filtered, washed and dried. Colorless needles melting at 66°–68.5°C are obtained on recrystallization from 100 ml of methanol. The yield is 42 percent.

##### B. 2,2'-Methylsulfonyliminobis(ethylisothiuronium chloride)

A mixture of 53.4 g (0.24 mole) of N,N-bis(2-chloroethyl)methanesulfonamide and 36.8 g (0.48 mole) of thiourea in 75 ml of tetramethylene sulfone is heated on a steam bath for 8 hours. The reaction mixture is cooled to room temperature, mixed with 150 ml of acetone and held in a refrigerator overnight. The mass of white crystals is filtered, washed with benzene and then with acetone. The test for residual thiourea is negative. A test with ammoniacal silver nitrate solution yields a bright yellow precipitate (not black silver sulfide) in the absence of thiourea. The crude product is recrystallized by dissolving it in 240 ml of hot methanol and then adding 960 ml of hot ethanol. The white crystals melt at 208°–210.5°C. The yield is 53.5 percent.

##### C. 2,2'-Methylsulfonyliminobis(ethylisothiuronium p-toluenesulfonate)

A solution of 16.5 g (0.06 mole) of silver tosylate in

250 ml of water is added to 11.0 g (0.03 mole) of 2,2'-methylsulfonyliminobis(ethylisothiuronium chloride) in 250 ml of water. The mixture is stirred for 20 minutes and filtered. The water is removed by evaporation at 50°C and the residue is recrystallized from ethanol. The product after drying over P<sub>2</sub>O<sub>5</sub> melts at 149°–155°C (dec.) and is slightly hygroscopic. The yield is 65.7 percent.

Analysis calculated for: C<sub>21</sub>H<sub>33</sub>N<sub>5</sub>O<sub>8</sub>S<sub>5</sub>  
C, 39.2; H, 5.2; S, 24.9  
Found: C, 38.9; H, 5.3; S, 24.5

The following composition is coated on a gelatin coated paper support at a coverage of 290 mg/ft<sup>2</sup> (silver coverage of coating is 21 mg/ft<sup>2</sup>):

|                                                                      |      |    |
|----------------------------------------------------------------------|------|----|
| Gelatin, bone, 12% by wt aqueous                                     | 50.0 | ml |
| 2,2'-Methylsulfonyliminobis-(ethylisothiuronium p-toluene-sulfonate) | 1.93 | g  |
| 1-Phenyl-3-pyrazolidone                                              | 1.0  | g  |
| Silver chloride photographic emulsion*                               | 4.5  | ml |
| 5-Methylbenzotriazole                                                | 0.1  | g  |

\*124 grams gelatin and 1 mole of silver in 2.33 kg emulsion.

After exposure, a strip of the coated paper is contacted, emulsion side up, for 15 seconds on a metal platen heated to 200°C. A brown-black image of good density is produced with a white background that is stable to the continued exposure of light. This example illustrates that stabilization takes place in the absence of added alkali.

### EXAMPLE 4

#### Incorporation of

#### 2,2'-methylsulfonyliminobis(ethylisothiuronium methanesulfonate)

Preparation of 2,2'-Methylsulfonyliminobis(ethylisothiuronium methanesulfonate):

##### A. N,N-Bis(2-mesyloxyethyl)methanesulfonamide

A solution of (1.0 g (1.0 mole) of diethanolamine (previously dried under dry nitrogen) and 334.0 g (3.3 moles) of triethylamine in 2.1 liters of tetrahydrofuran is cooled to 0°C in an ice bath. Methanesulfonyl chloride (343.7 g, 3.0 moles) is added dropwise at 0°–5°C, with vigorous stirring, within 2.5 hours. The pale yellow solid formed is collected by filtration. It is then stirred with 3 liters of distilled water for one-half hour, filtered, and washed with water. The white solid is dissolved in 2 liters of acetone and dried. After adding 750 ml of chloroform, the solution is allowed to cool slowly to room temperature. The colorless crystals are collected and recrystallized again from an acetone and chloroform mixture. A yield of 154 g (45 percent) of colorless crystals melting at 114.5°–116°C is obtained.

##### B. 2,2'-Methylsulfonyliminobis(ethylisothiuronium methanesulfonate)

A mixture of 142.5 g (0.42 mole) of N,N-bis-(methanesulfonyloxyethyl)methanesulfonamide, 64.3 g (0.845 mole) of thiourea and 140 ml of tetramethylene sulfone is stirred and heated on a steam bath for 4

hours. At the end of this period, the solution has solidified into a mass of white crystals. After cooling to room temperature, the white solid is broken up and washed with acetone until a negative test for thiourea is obtained. The crude product is recrystallized from 2.5 liters of a mixture of methanol and ethanol (1:1) after drying. The white, crystalline product is collected and washed with acetone, followed by ethyl acetate. The yield of product is 135 g (66 percent), melting at 155°–158°C.

The following composition is coated on gelatin coated paper base at a coverage of 290 mg/ft<sup>2</sup> (silver coverage on coating is 21 mg/ft<sup>2</sup>):

|                                                                   |      |    |
|-------------------------------------------------------------------|------|----|
| Gelatin, bone, 12% by wt aqueous                                  | 50.0 | ml |
| 2,2'-Methylsulfonyliminobis-(ethylisothiuronium methanesulfonate) | 1.48 | g  |
| 1-Phenyl-3-pyrazolidone                                           | 1.0  | g  |
| Urea                                                              | 2.0  | g  |
| Silver chloride photographic emulsion*                            | 4.5  | ml |
| 5-Methylbenzotriazole                                             | 0.1  | g  |

\*contains 124 g gel and 1 mole of silver in 2.6 kg emulsion.

After exposure, a strip of the coated paper with the side opposite the emulsion coating is heated for 15 seconds on a metal platen heated to 160°C. A greenish-black image of good density is produced with a white background that is stable to the continued exposure to light. This example illustrates that the processing may be carried out at lower temperature in the presence of an alkali precursor such as urea.

#### EXAMPLE 5

##### Incorporation of Mono-Isothiuronium Sulfonyl Salt

##### Preparation of 3-Methylsulfonylpropylisothiuronium trifluoroacetate:

##### A. 3-Methylsulfonylpropylisothiuronium Chloride

A mixture of 18.8 g (0.12 mole) of 3(methylsulfonyl)propyl chloride and 9.1 g (0.12 mole) of thiourea in 100 ml of ethanol is refluxed for 4 hours. On cooling to room temperature, the reaction mixture gives a positive test for thiourea. Tetramethylenesulfone (5 ml) and a few crystals of potassium iodide are added and the mixture is refluxed for 15 hours. The reaction mixture is then cooled to room temperature. On standing for a short period, a white solid is formed. The mixture is reheated to reflux for 15 minutes, cooled to room temperature (20°C) and then cooled in an ice bath for 30 minutes. The resulting white solid is filtered, washed with 20 ml of ethanol and then with acetone until a negative test for thiourea is obtained. White crystals melting at 156°–159°C are obtained by recrystallization from a mixture of 300 ml ethanol and 60 ml methanol

and drying under vacuum at 40°C for 2 hours. The yield is 51.2 percent.

##### B. 3-Methylsulfonylpropylisothiuronium Trifluoroacetate

A solution of 13.24 g (0.06 mole) of silver trifluoroacetate in 30 ml of water is added to a solution of 14.0 g (0.06 mole) of 3-methylsulfonylpropylisothiuronium chloride in 50 ml of water. Silver chloride precipitates immediately. After standing at room temperature for 30 minutes, the silver chloride is removed by gravity filtration and washed with about 15 ml of water. The wash water and filtrate are combined and evaporated at 60°C. The white solid residue is recrystallized from 50 ml of a mixture of ethyl acetate and acetone (3:1). The needlelike crystals are dried over P<sub>2</sub>O<sub>5</sub> for 3 hours, melting at 157°–161°C. The yield is 50 percent.

Analysis calculated for: C<sub>7</sub>H<sub>7</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>:  
C, 27.1; H, 4.2; S, 20.6; F, 18.4  
Found: C, 26.9; H, 4.1; S, 20.8; F, 18.6

The procedure and coating composition of Example 4 are repeated using 1.55 grams of 3-methylsulfonylpropylisothiuronium trifluoroacetate in place of the 1.48 grams of methylsulfonyliminobis(ethylisothiuronium methanesulfonate).

After the exposed paper coating is heated for 15 seconds at 160°C, an image of good density with a greenish-black hue is produced and a background that is stable to continued light exposure.

#### EXAMPLE 6

##### Comparative Example of Lower Temperature Stabilization

The emulsion compositions shown in Table II are coated at about 40 mg/ft<sup>2</sup> on polyester film base.

The stabilizing agents are present in compositions 2 and 4 at 0.01 molecular weight and in composition 3 at 0.005 (the stabilizer in 3 contains two isothiuronium groups and is used at one-half the quantity of 2 and 4 in order to maintain equivalence).

Strips of coatings 1–4 are sensitometrically exposed. Each strip is then pressed, emulsion side up, for 15 seconds against a heated metal block that is at a temperature of 160°C.

Image development occurs quickly with coatings 1 (no stabilizer) and 4 [bis(methylsulfonyl)methane], but very high background fog obscures the image. This production of fog indicates a lack of silver complexing action, needed also to produce light-stable images.

Coating 2 (3-S-thiuroniumpropane sulfonate) produces a silver image of good density and free of background fog, indicating some stabilizing or antifogging action. This action is insufficient, however, at this temperature (160°C) to stabilize

TABLE II

| Ingredient                                                         |    | Coating Composition |      |      |      |
|--------------------------------------------------------------------|----|---------------------|------|------|------|
|                                                                    |    | 1                   | 2    | 3    | 4    |
| Gelatin, pigskin, 12% by wt aqueous                                | ml | 50.0                | 50.0 | 50.0 | 50.0 |
| Alkylphenoxypoly(Hydroxypropylene oxide)                           |    |                     |      |      |      |
| Surfactant, 10% by wt., aqueous                                    | ml | 1.0                 | 1.0  | 1.0  | 1.0  |
| 3-S-Thiuronium propane sulfonate                                   | g  |                     | 2.0  |      |      |
| 2,2'-Methylsulfonyliminobis(ethylisothiuronium p-toluenesulfonate) | g  |                     |      | 3.4  |      |

TABLE II—Continued

| Ingredient                            |    | Coating Composition |     |     |     |
|---------------------------------------|----|---------------------|-----|-----|-----|
|                                       |    | 1                   | 2   | 3   | 4   |
| Bis(methylsulfonyl)methane            | g  |                     |     |     | 1.7 |
| D-Galactonamide                       | g  | 3.0                 | 3.0 | 3.0 | 3.0 |
| 1-Phenyl-3-pyrazolidone               | g  | 1.0                 | 1.0 | 1.0 | 1.0 |
| 5-Methylbenzotriazole                 | g  | 0.2                 | 0.2 | 0.2 | 0.2 |
| Silver chloride photographic emulsion | ml | 9.0                 | 9.0 | 9.0 | 9.0 |

the image, as the background quickly darkens when the strip is brought into the light (room light and daylight).

Coating 3, containing 2,2'-methylsulfonyliminobis (ethylisothiuronium p-toluenesulfonate), a compound of the invention, produces a light-stable image of good density, free from fog and not affected by continued light exposure. This compound is thus superior to the other two in that it will stabilize effectively at 160°C.

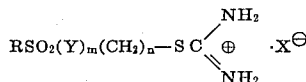
The invention has been described with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A photographic element comprising a support having thereon

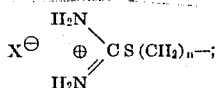
a. a silver halide photographic emulsion and associated therewith

b. a stabilizer precursor which is a sulfonylalkyl or sulfonamidoalkyl isothiuronium compound having the formula:



wherein

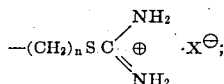
R = alkyl having one to five carbon atoms, aryl having 6–12 carbon atoms or



Y = NR' or ZSO<sub>2</sub>;

Z = a divalent hydrocarbon radical having one to five carbon atoms or a carbon chain containing —C—O—C—;

R' = H, alkyl having one to five carbon atoms or

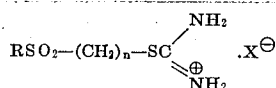


m = 0 or 1;

n = 2 or 3 and

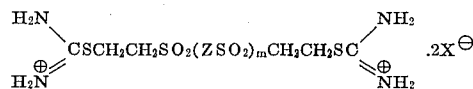
X<sup>−</sup> is a non-metallic acid anion.

2. An element of claim 1 in which said isothiuronium compound has the following formula:



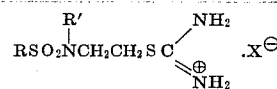
where R is alkyl having one to five carbon atoms or aryl having 6–12 carbon atoms, X<sup>−</sup> is a non-metallic acid anion, and n is 2 or 3.

3. An element of claim 1 in which said isothiuronium compound has the formula:



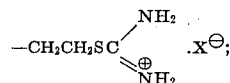
20. where Z is a divalent hydrocarbon radical having one to five carbon atoms or a carbon chain containing —C—O—C—, m is 0 or 1 and X<sup>−</sup> is a non-metallic acid anion.

4. An element of claim 1 in which said isothiuronium compound has the formula:



30. where

R' is H, alkyl having one to five carbon atoms or

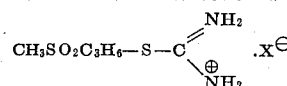


R is alkyl having one to five carbon atoms or aryl having 6–12 carbon atoms and X<sup>−</sup> is a non-metallic anion.

5. An element as in claim 1 wherein said element contains an incorporated developing agent.

6. An element of claim 1 wherein said element contains a stabilization activator precursor.

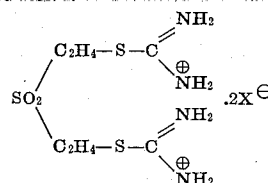
7. An element of claim 1 wherein said stabilizer precursor is an isothiuronium compound represented by the formula:



where

X<sup>−</sup> is a halide, tosylate, or mesylate ion.

8. An element of claim 1 wherein said stabilizer precursor is an isothiuronium compound represented by the formula:

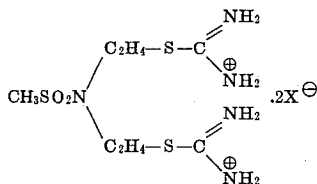


where

X<sup>−</sup> is a halide, tosylate, or mesylate ion.

13

9. An element as in claim 1 wherein said stabilizer precursor is an isothiuronium compound represented by the formula:

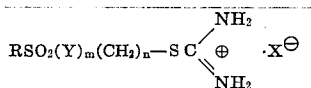


where

$\text{X}^-$  is a halide, tosylate, or mesylate ion.

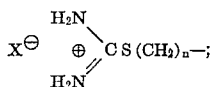
10. In a substantially dry stabilization process which comprises heating at a temperature above about 90°C an exposed photographic element comprising

- a silver halide photographic emulsion and associated therewith
- a stabilizer precursor, the improvement which comprises utilizing as said stabilizer precursor a sulfonalkyl or sulfoamidoalkyl isothiuronium compound having the formula:



wherein

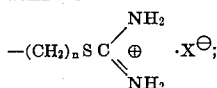
R = alkyl having one to five carbon atoms, aryl having 6–15 carbon atoms or



Y = NR' or ZSO<sub>2</sub>;

Z = a divalent hydrocarbon radical having one to five carbon atoms or a carbon chain containing —C—O—C—;

R' = H, alkyl having one to five carbon atoms or

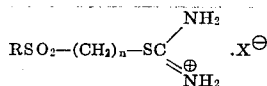


m = 0 or 1;

n = 2 or 3 and

$\text{X}^-$  is a non-metallic acid anion.

11. A process of claim 10 in which the isothiuronium compound has the formula:

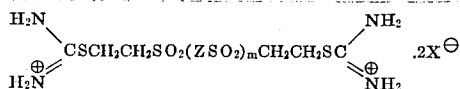


where

R is alkyl having one to five carbon atoms or aryl having 6–12 carbon atoms,

$\text{X}^-$  is a non-metallic acid anion, and n is 2 or 3.

12. A process of claim 10 in which the isothiuronium compound has the formula:

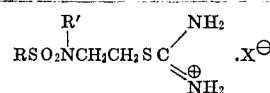


where

14

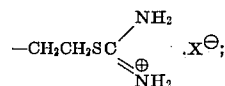
Z is a divalent hydrocarbon radical having one to five carbon atoms or a carbon chain containing —C—O—C—; m is 0 or 1 and  $\text{X}^-$  is a non-metallic acid anion.

13. A process of claim 10 in which the isothiuronium compound has the formula:



where

R' is H, alkyl having one to five carbon atoms or

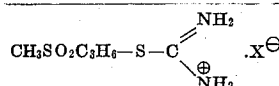


R is alkyl having one to five carbon atoms or aryl having 6–12 carbon atoms and  $\text{X}^-$  is a non-metallic acid anion.

14. A process as in claim 10 wherein said element contains an incorporated developing agent.

15. A process as in claim 10 wherein said element contains a stabilization activator precursor.

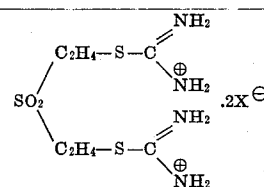
16. A process as in claim 10 wherein said stabilizer precursor is an isothiuronium compound represented by the formula:



where

$\text{X}^-$  is a halide, tosylate, or mesylate ion.

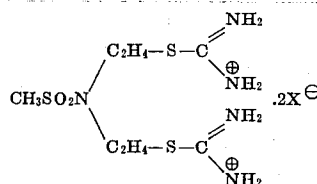
17. A process as in claim 10 wherein said stabilizer precursor is an isothiuronium compound represented by the formula:



where

$\text{X}^-$  is a halide, tosylate, or mesylate ion.

18. A process as in claim 10 wherein said stabilizer precursor is an isothiuronium compound represented by the formula:



where

$\text{X}^-$  is a halide, tosylate, or mesylate ion.

19. A process as in claim 10 wherein said heating is carried out at temperatures of from about 90°C to about 260°C.

15

20. A process as in claim 10 wherein said heating is carried out for a period of from about 1 to about 20 seconds.

21. A process as in claim 10 wherein said heating is carried out at temperatures of from about 90°C to about 260°C for a period of from about 1 to about 20 seconds in the presence of a silver halide developing agent and a stabilization activator precursor.

16

22. A process as in claim 10 wherein said heating is carried out at temperatures of at least about 90°C for a period of from about 1 to about 20 seconds in the presence of a mixture of a hydroquinone developing agent, a 3-pyrazolidone developing agent, and a guanidinium organic acid salt, urea or galactonamide stabilization activator precursor.

\* \* \* \* \*

10

15

20

25

30

35

40

45

50

55

60

65