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3,506,444

DRY STABILIZATION OF PHOTOGRAPHIC IMAGES

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U.S. Cl. 96—61

10 Claims

ABSTRACT OF THE DISCLOSURE

Method of stabilizing a photographic silver halide element with certain isothiourea derivative stabilizer precursors, such as 3-S-thiuronium propane sulfonate, which are activated with the aid of heat.

The present invention comprises a substantially dry stabilization method which comprises heating at temperatures of at least about 90° C. an exposed photographic silver halide element comprising a photographic silver halide emulsion and, contiguous to said silver halide, an active amount of an isothiourea derivative, to produce a stabilized element which is essentially free of objectionable odor.

After an exposed photographic silver halide emulsion is developed and a silver image produced in the exposed areas, the silver halide in the unexposed areas is commonly removed by treatment with sodium thiosulphate or other fixing solutions to produce a soluble silver compound when a permanent silver image is desired. It is possible to stabilize the unexposed and undeveloped silver halide by reaction with a compound that forms a silver salt or complex that is colorless or relatively light in color and resistant to print-out. It is often convenient to incorporate a fixing or image stabilizing agent as an integral part of the photographic element. However, commonly used fixing agents are often not suitable for use in layers contiguous to photographic silver halide because they react with the silver halide in unexposed form and render the emulsion useless for photographic purposes.

It has been proposed to add a fixing or stabilizing agent as an integral part of a photographic element which can be readily activated at elevated temperatures. So-called precursor compounds which produce fixing agents under certain conditions have been proposed heretofore. However, many such precursors or fixing agents which may be compatible with photographic silver halide emulsions either cannot be activated at elevated temperatures at which conventional photographic silver halide emulsions can be processed or they are prematurely activated at temperatures of conventional use and storage.

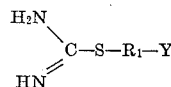
Many attempts heretofore have been made to produce a photographic process for stabilizing photographic images under substantially dry conditions with the aid of heat. However, up to the present time, no system has been proposed which is entirely satisfactory.

Certain isothiourea derivatives have been proposed for such purposes in Humphlett et al., Ser. No. 371,124, filed May 28, 1964, now U.S. Patent 3,301,678. However, these compounds have not been found entirely satisfactory due to their obnoxious odor.

According to the present invention, an exposed photographic silver halide may be stabilized by a process wherein a sulfur-containing isothiourea derivative is incorporated in a photographic silver halide element. The isothiourea derivative of the invention is a so-called precursor which breaks down at elevated temperatures to form a compound which combines with the silver halide in the unexposed areas of the emulsion to form a mer-

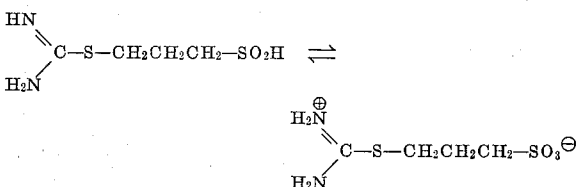
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captide compound which is more stable to light, atmospheric and ambient conditions than silver halide. The isothiourea derivative of the process of the invention may be represented by the structure:

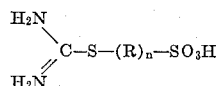


wherein R₁ is an alkylene or alkyl or aryl substituted alkylene radical such as alkyl or phenyl substituted alkylene radical, lower alkyl or phenyl substituted radicals including an ethylene, propylene or butylene radical and methyl or phenyl substituted propylene or butylene radical. Y is an anion, or acid radical, such as —SO₃H, which form a so-called inner acid salt. Y is preferably a sulfonate radical forming an inner acid salt with the isothiuronium moiety of the above structure.

Inner salts within the scope of the above structure can be represented by the equation:



One embodiment of the invention comprises a substantially dry stabilization method which comprises heating at a temperature above about 90° C. to about 260° C., an exposed photographic silver halide element comprising a silver halide emulsion in the presence of an active stabilizing amount of sulfoalkyl thiopseudo urea, also known as thiuronium alkane sulfonate, represented by the structure:



wherein R is an alkylene radical and n is an integer of at least 1, preferably 1 to about 4.

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 conventional storage and use of photographic products. These compounds do not break down or cause adverse photographic effects in the absence of elevated temperatures or activating amounts of alkalis. However, 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.

In the process of the invention, the isothiourea derivatives can be activated at a temperature above about 90° C. and preferably above about 150° C. The temperature range at which the derivatives are treated will be determined by the various components of the emulsion, the developing agent and activator employed, the degree of development or stabilization desired and other factors including the type of support and photographic emulsion. Heating, in general, can be conveniently carried out by contact of the photographic element containing the isothiourea compound with heated rollers, plates, or other heated carrier means, with steam, infra-red radiation, or by any other suitable means for effecting the desired temperatures.

The time or period of heating in the present process can be varied widely. Factors such as the temperature

employed and the ease of heat cleavability of the fixing or stabilization agent employed and other factors will determine the duration of the heating step. Generally, however, the heating period ranges from about 1 to about 5 seconds and is preferably as short as possible to produce the desired stabilization. The optimum heating period considering temperature, development, fixing, stabilizing and other factors can be readily determined by those skilled in the art.

The isothiourea derivatives are utilized in the present process typically at concentrations of at least $\frac{1}{4}$ mole of the isothiourea derivative for each mole of the silver halide present in the emulsion, suitably $\frac{1}{4}$ to about 20 moles of the isothiourea for each mole of silver halide. However, it is preferable to utilize molar excesses of the isothiourea derivatives 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 isothiourea derivatives 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% 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. Large amounts of water, however, are to be avoided and have an adverse effect on the present process.

The isothiourea derivatives 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 chloriodide, or mixed silver halides such as silver chlorobromide or silver bromiodide.

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 and 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

ble 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 antifoggants, plasticizers, toners, coating aids, development restrainers, buffers and hardeners. Sensitizing dyes may have also been 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 isothiourea 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. Patent 2,322,027—Jelley et al., and U.S. Patent 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 Patent 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 isothiourea derivatives to form a compound which combines with the unexposed silver halide of a photographic silver halide emulsion.

Suitable activators need not be incorporated activators in the silver halide emulsion or silver halide element. Inorganic alkalis 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 $\frac{1}{4}$ 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 $\frac{1}{2}$ 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.

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Since the isothiurea compounds can be activated by these inorganic alkalis, it is usually desirable not to contact the isothiurea compounds according to the process of the invention with such inorganic 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 isothiurea derivatives, 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 isothiurea derivatives. 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 amino caproic acid; hydrazide compounds, such as benzhydrazide and isonicotinic acid hydrazide. Suitable activator precursors are set out, for example, in British Patent 930,572.

The present invention is further illustrated by the following examples:

EXAMPLE 1

3-S-thiuronium propane sulfonate

A white paper photographic support having a gelatin layer coating, coated at the rate of 270 mg. per square foot, was coated with a solution, at the rate of 10 grams per square foot, containing the following composition:

	Grams/liter
t-butyl hydroquinone	5.0
4-methyl-4-hydroxymethyl - 1 - phenyl - 3-pyrazolidone	4.5
3-S-thiuronium propane sulfonate	50.0
Guanidinium trichloroacetate	60.0
Polyvinyl alcohol	27.0
Alcohol	100.0
Water to make 1 liter.	

After drying at 40° C., the element was further coated in the dark with a slow projection speed silver chloride photographic emulsion at a coverage of 50 mg. per square foot of silver and 57 mg. per square foot of gelatin. Strips of the above prepared light-sensitive coatings were exposed to a line image and a photographic step tablet using conventional tungsten light. The exposed element was then brought into contact with a heated metal block at 190° C. After 2 seconds, a visible image having a maximum density of 1.2 was completely developed and stabilized. Exposure of the thus processed paper to daylight fluorescent light at 250 foot-candles for 1 hour caused no visible change in the image.

EXAMPLE 2

The process of Example 1 was repeated employing the same compositions as set out in Example 1 with the exception that the coating containing t-butyl hydroquinone and 3-S-thiuronium propane sulfonate was applied to the initial gelatin layer after the slow projection speed silver chloride emulsion was applied. Similar results were obtained to those in Example 1.

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EXAMPLE 3

A white paper photographic support was coated at the rate of 10 grams per square foot with a composition comprising:

	Grams/liter
Polyvinyl alcohol	48.0
t-Butyl hydroquinone	3.1
4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone	3.1
3-S-thiuronium propane sulfonate	31.0
Diguanidinium oxalate	52.0
Ethyl alcohol	100.0
Water to make 1 liter.	

A silver chlorobromide emulsion containing 40 mg. per square foot of silver and 120 mg. per square foot of gelatin was coated over the above layer. After exposure, pieces of the coatings were fully developed and stabilized by heating them at 220° C. for 2 seconds.

EXAMPLE 4

Coatings were prepared employing the procedure and compositions of Example 3 with the exception that the diguanidinium oxalate was replaced with one of the alkaline activator precursor compounds set out in Table I. In each case, the amounts by weight used were equal to that set out in Example 3 for diguanidinium oxalate.

TABLE I.—Activator Precursors for Dry Processing

Compounds	A		C
	Time (sec)	Processing temp., °C	Maximum density
Guanidine salts:			
Diguanidinium glutarate	4	190	1.31
Diguanidinium succinate	2	190	1.17
Diguanidinium malonate	2	190	1.00
Diguanidinium maleate	8	190	1.13
Diguanidinium fumarate	8	190	1.22
Monoguanidinium malonate	4	220	0.94
Monoguanidinium succinate	4	220	1.10
Diguanidinium adipate	4	190	1.25
Diguanidinium pimelate	2	190	1.25
Diguanidinium itaconate	4	190	1.23
Triguanidinium citrate	8	190	1.13
Malonates:			
N-isopropylcyclohexylamine malonate	p4	220	0.68
N,N'-diethylethylenediamine bismalonate	p4	220	0.67
Pyrrolidine malonate	p4	220	0.76
Piperidinium malonate	p4	220	0.59
Piperazinium malonate	2	190	0.85
Monacetamidinium malonate	2	220	1.01
2-diethylaminoethylamine malonate	2	190	0.90
Amino acids:			
4-aminobutyric acid	2	190	1.05
6-aminocaproic acid	2	190	1.03
D,L-beta-amino-n-butyric acid	8	190	1.05
Glycine	4	220	0.94
Beta-alanine	8	190	1.08
D,L-serine	4	220	0.81
Hydrazides:			
Benzhydrazide	2	220	0.63
o-Aminobenzhydrazide	8	190	0.89
Isonicotinic acid hydrazide	2	220	0.63
N-methylpiperidinebenzimidate	4	220	0.61
Miscellaneous:			
Oxazolidone	p4	220	0.80
N-methyloxazolidone	p4	220	0.80
Tetramethylammonium fumarate	8	190	0.90
Sodium trichloroacetate	2	220	1.00

P—Indicates partial stabilization at given time and temp.

In each instance, results similar to that achieved in Example 3 were observed. The time suitable for obtaining a developed stabilized image is given in column A of Table I. The temperature employed to achieve the desired image and the maximum density achievable are given respectively in columns B and C of Table I.

EXAMPLE 5

The procedure set out in Example 4 was repeated with the exception that the light-sensitive silver halide emulsion was applied to the support below the layer containing the processing chemicals. The results achieved with this procedure were substantially the same as those observed in the prior examples.

EXAMPLE 6

A gelatin coating solution was prepared containing the following components:

Gelatin (15%)—20.00 ml.
Water—20.00 ml.
2-S-thiuronium ethane sulfonate—2.00 g.
Sucrose—2.00 g.
Hydroquinone—0.75 g.
Silver chloride emulsion—2.20 g.

After mixing and adding a spreading agent the solution was filtered and coated under safe light conditions on a white baryta paper support. After drying at 120° F., the coating was exposed and processed by contacting the back of the paper support with a heated block at 200° C. for about 5 seconds. No objectionable odor could be observed and the image was developed and stabilized with a $D_{\max}$ of about 0.8. The stabilized coatings were then subjected to 45 foot-candles of illumination for 8 hours. No change in the coatings was observed.

EXAMPLE 7

The procedure set out in Example 6 was repeated with the exception that 3-S-thiuronium propane sulfonate was employed in place of the 2-S-thiuronium ethane sulfonate. Similar results were obtained to those set out in Example 6.

EXAMPLE 8

The procedure set out in Example 6 was repeated with the exception that 4-S-thiuronium butane sulfonate was employed in place of 2-S-thiuronium ethane sulfonate. Similar results were obtained to those in Example 6.

EXAMPLE 9

The procedure set out in Example 6 was repeated with the exception that 3-S-thiuronium 3-methyl propane sulfonate was employed in place of 2-S-thiuronium ethane sulfonate. Similar results were obtained to those set out in Example 6.

EXAMPLE 10

The procedures set out in Examples 6, 7, 8 and 9 were repeated with the exception that in each case 2 grams of guanidinium thichloroacetate was added to the coating solution before application to the paper support. The results obtained in each instance were substantially the same as those obtained in Examples 6-9 with the exception that $D_{\max}$ in each case was increased to about 1.0.

This demonstrates that it is possible to obtain stabilization employing the stabilization precursor of the invention in the absence of a stabilization activator precursor or alkali. However, this also demonstrates that better results such as increased maximum density and speed of processing can be achieved if the stabilization activator precursor is employed in the processing composition.

EXAMPLE 11

A coating solution was prepared containing the following components:

Glacial acetic acid—4.0 ml.
Gelatin—20.0 ml.
Betaine hydrate—2.0 g.
1-phenyl-3-pyrazolidone—0.2 g.
Ascorbic acid—0.4 g.
 β -(2-morpholinoethylthio) - β -phenyl-p-methoxypropio-phenone hydrochloride—2.0 g.
Water—16.0 ml.

After mixing the above components and adding 2 ml. of a surfactant, the resulting solution was coated at the thickness of 0.004 inch on a silver chloride emulsion coating on a baryta paper support. The resulting coating was allowed to dry and then a portion thereof was ex-

posed to white light through a step tablet. The exposed coating was then processed by pressing the side of the paper support opposite the emulsion layer against a metal sheet heated to 130° C. for 15 seconds. During the coating and processing steps, a strong, pungent mercaptide odor was clearly present. Such odor especially during the heat processing step is particularly undesirable. The processed area of the resulting element was then subjected to 250 foot-candles of illumination for a period of one hour.

Similar coatings were made and processed employing the same procedure with the exception that 2-hydroxy-ethylisothiourea chloride was employed in place of the above hydrochloride compound. Similar results were produced. A strong, pungent mercaptide odor was evident during the processing period.

The procedures were again repeated with the exception that 3-S-thiuronium propane sulfonate was employed in place of the above chloride and hydrochloride compounds. The concentrations of each component were the same during the preparation of the coating. No undesirable odor was observed. Upon heating the resulting element at 190° C. for 2 seconds, the resulting coating was stabilized against print-out to light. No undesirable odor was present during heating and the resulting stabilized element had no undesirable odor.

In determining the degree of stabilization which is suitable for the process of the invention, a standard was set whereby the elements produced were exposed to heat for a few seconds and then subsequently exposed to 250 foot-candles of day-light fluorescent light for 1 hour. If the resulting exposed element showed less than 0.05 change in density from the originally unexposed area of the processed element, the element was considered stable.

The temperature for processing a given coating will effect the time required to produce a stable element. The following example illustrates, however, that a range of temperatures is suitable for the process of the invention.

EXAMPLE 12

A silver chloride photographic emulsion coating, containing 30 mg. per square foot of silver in gelatin, was applied to a white baryta paper support. The resulting layer was then coated at the rate of 9.5 grams per square foot with a polyvinyl alcohol layer containing the following components:

	Grams/liter
Polyvinyl alcohol	20.0
t-Butyl hydroquinone	5.0
4 - methyl - 4 - hydroxymethane - 1 - phenyl - 3 - pyrazolidone	5.0
3-S-thiuronium propane sulfonate	50.0
Diguanidinium oxalate	85.0
Ethyl alcohol	100.0

After drying the coatings were exposed through a photographic step tablet to tungsten light and a series of strips each measuring about 1" by 7" was held in contact with a heated plate at a range of temperatures for periods of 2, 4 and 8 seconds. The surface for each sample contacted with the heated plate was the surface opposite that having the emulsion layer. Temperatures between 190° C. and 220° C. produced stabilization in each instance.

EXAMPLE 13

The following procedure demonstrates the various operable concentration ranges which can be employed in the stabilization process of the invention.

A white baryta paper support was coated with an emulsion containing 23 ml. per square foot of silver. A processing layer was coated over the resulting emulsion layer at the rate of 9.5 g. per square foot. The processing layer

was applied as an aqueous solution containing the following components:

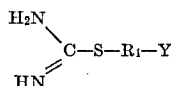
	Grams/liter
Polyvinyl alcohol -----	20.0
t-Butyl hydroquinone -----	5.0
4 - methyl - 4 - hydroxymethyl - 1 - phenyl - 3 - pyrazolidone -----	5.0
3-S-thiuronium propane sulfonate -----	2.5-60.0
Guanidinium trichloroacetate -----	60.0
Ethyl alcohol -----	100.0
Water to make 1 liter.	

After drying, portions of the resulting element were exposed through a step tablet to tungsten light and then processed by holding the side of the paper support opposite the processing layer in contact with a metal plate for a few seconds at 190° C. Stabilization of the processed image to effects of light was determined by exposing the resultant element to 250 foot-candles of daylight fluorescent light for one hour and noting any density change in the areas which originally had no exposure to light. In tests employing the above procedure 0.6, 1.2, 3.6, 7.2, 10.8 and 14.4 moles of 3-S-thiuronium propane sulfonate were employed per mole of silver in the emulsion layer for a series of samples. No density changes greater than 0.05 were observed in the resulting products after heat processing at 2, 4, or 8 seconds.

Although the invention has been described in considerable detail with reference to certain preferred 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.

We claim:

1. A substantially dry stabilization method which comprises heating at a temperature above about 90° C. an exposed photographic element comprising a photographic emulsion containing silver halide and, contiguous to said silver halide, a stabilizer precursor represented by the structure:



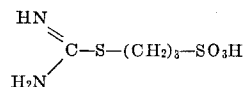
wherein R₁ is selected from the group consisting of alkylene, alkyl substituted alkylene and aryl substituted alkylene radicals; Y is selected from the group consisting of anions and acid radicals which form an inner acid salt, said compound upon said heating forming an organic thiol which combines with unexposed silver halide to form a silver mercaptide which is more stable to light than said silver halide.

2. A process as in claim 1 wherein said element contains an incorporated developing agent.

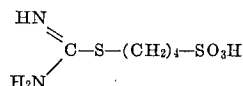
3. A process as in claim 1 wherein said element contains a stabilization activator precursor.

4. A process as in claim 1 wherein Y is a sulfonate radical.

5. A process as in claim 1 wherein said stabilizer precursor is an isothiurea derivative represented by the structure:



6. A process as in claim 1 wherein said stabilizer is an isothiurea derivative represented by the structure



7. A process as in claim 1 wherein said heating is carried out at temperatures of about 190° C. to about 260° C.

8. A process as in claim 1 wherein said heating is carried out for a period of about 1 to about 5 seconds.

9. A process as in claim 1 wherein said heating is carried out at temperatures of about 190° C. to about 260° C. for a period of about 1 to about 5 seconds in the presence of a silver halide developing agent and a stabilization activator precursor.

10. A process as in claim 1 wherein said heating is carried out at temperatures of about 190° C. to about 260° C. for a period of about 1 to about 5 seconds in the presence of a mixture of a hydroquinone developing agent and a 3-pyrazolidone developing agent and a guanidinium organic acid salt stabilization activator precursor.

References Cited

UNITED STATES PATENTS

3,140,178	7/1964	Herz et al.	96-61
3,189,453	6/1965	Herz et al.	96-61
3,220,839	11/1965	Herz et al.	96-61
3,301,678	1/1967	Humphlett et al.	96-61
3,306,884	2/1967	Dykstra et al.	260-79.7

NORMAN G. TORCHIN, Primary Examiner

A. T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

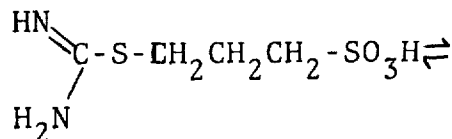
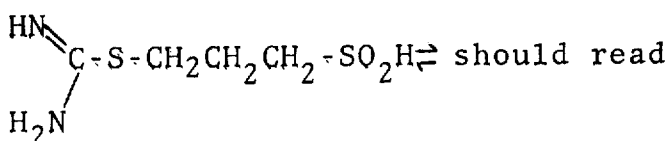
Patent No. 3,506,444

Dated April 14, 1970

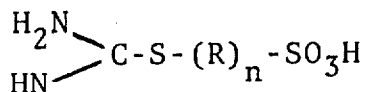
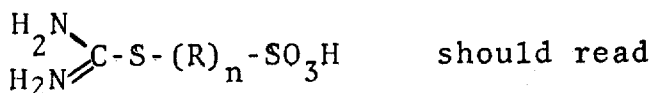
Inventor(s) Grant M. Haist et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 20,



line 36,



Column 7, line 32, "2-Sthiuronium" should read -- 2-S-thiuronium --.

Signed and sealed this 29th day of December 1970.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents