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3,535,115

SILVER HALIDE SYSTEMS CONTAINING STABILIZER PRECURSORS

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U.S. Cl. 96—109

18 Claims

ABSTRACT OF THE DISCLOSURE

A silver halide system containing silver halide grains having polyvalent ions occluded therein, said silver halide system comprising a halogen acceptor and a stabilizer precursor. In one embodiment silver halide print-out emulsions contain stabilizer precursor materials which do not substantially repress the photolytic yield or print-out density until after they are decomposed or transposed to an active form.

This invention relates to radiation-sensitive silver halide materials. In one aspect this invention relates to a print-out silver halide composition containing silver halide grains with occluded polyvalent metal ions therein and having a halogen acceptor and a stabilizer precursor adjacent to said grains. In another aspect this invention relates to a print-out emulsion with improved background color and improved stability with respect to the effect of moisture on the image record. In still another aspect this invention relates to a process for obtaining image records with improved image properties.

Emulsions which have good print-out characteristics are generally known in the art. In one instance, emulsions of this type generally contain silver halide grains which have been precipitated in the presence of polyvalent metal ions. French Pat. 1,456,581 made available Oct. 28, 1966, discloses several emulsions of this type.

It is desirable to improve the image characteristics of emulsions of the type containing silver halide grains having polyvalent metal ions occluded therein. In some instances it is desirable to reduce the sensitivity of said emulsion to moisture; the background of the image record can become discolored where it is subjected to high humidity or moisture, such as that from fingerprints. It is also desirable to control D_{min} at a low level and reduce background coloration after formation of an image record when exposed for long periods in room light. Reduction of background color is especially important where copies are to be made of the image record as many copying techniques cannot distinguish between black silver images and dark background colors.

Therefore, it is an object of this invention to provide new radiation-sensitive emulsions.

It is another object of this invention to provide new radiation-sensitive emulsions which can be used to prepare visible images directly by exposure to light.

It is another object of this invention to provide novel radiation-sensitive emulsions with improved stability with respect to moisture.

It is another object of this invention to provide novel radiation-sensitive emulsions with light or neutral background color.

It is another object of this invention to provide novel radiation-sensitive emulsions which will provide images with low D_{min} upon prolonged exposure to light.

It is still another object of this invention to provide novel silver halide systems that can be used in a photo-development process.

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It is still another object to provide a means for providing improved image records in radiation-sensitive silver halide emulsions containing silver halide grains with polyvalent metal ions occluded therein.

I have now discovered that these and other objects are accomplished with a radiation-sensitive silver halide system containing (1) silver halide grains having polyvalent metal ions or atoms occluded therein, (2) a heat-resistant halogen acceptor and (3) a stabilizer precursor. In one embodiment the emulsion further contains a stabilizer activator. In one embodiment the silver halide grains are precipitated in the presence of trivalent metal ions. In another embodiment the stabilizer precursor is a compound which will reduce the tendency of the background to increase in density upon exposure to light after heating to temperatures of above about 90° C.

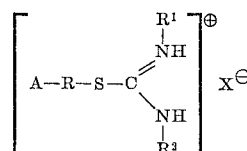
The stabilizer precursor materials generally useful according to this invention include those compounds which have low stabilizing activity until after they have been treated by an activator compound such as a free base, heat or similar means whereby the precursor breaks down or transposes to an active form. Preferred stabilizer precursor materials useful according to this invention include those compounds which do not substantially repress the photolytic yield of photolytic density of a print-out silver halide emulsion until they have been heated to their transition temperature of at least about 90° C. wherein they are decomposed or transposed to an active form such as a free mercaptan. In one preferred embodiment the stabilizer precursors are thio compounds having at least one alkyl group attached to the thio atom. Stabilizer precursors of this type generally cleave to form mercapto alkyl compounds even when the thio atom is attached to a cyclic group through the remaining valence. In still a more preferred embodiment the stabilizer precursors are linear sulfur containing compounds, i.e., those which contain no cyclic groups.

It is quite unexpected that these stabilizer precursors can be used to increase the legibility of the image record of a silver halide emulsion coating which contains silver halide grains having polyvalent ions occluded therein, especially in applications wherein the visible image record is obtained through photodevelopment. It is known to use several of the stabilizer precursors, which are useful in the present invention, in developing-out type emulsions wherein a developing agent is contacted with the exposed silver halide; the stabilizer precursor is heated to transpose the compound and react with the silver halide wherein any further development of the unexposed silver halide will be terminated. Therefore, it is quite unexpected that certain silver halide emulsions containing these stabilizers exhibit substantial visible print out or formation of photolytic density after activation of the stabilizer precursor.

The stabilizer precursors are utilized in the emulsions of this invention in concentrations of generally about .001 mole to about 1 mole per mole of silver halide and preferably from about .01 mole to about .1 mole per mole of silver halide.

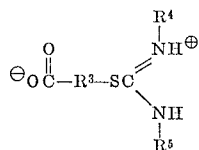
Suitable stabilizer precursors include the compounds of Humphlett et al., U.S. Pat. 3,301,678 issued Jan. 31, 1967. These compounds are generally represented by the following formulas:

Formula A

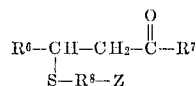


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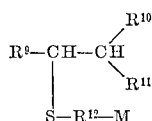
Formula B



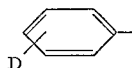
Formula C



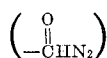
Formula D



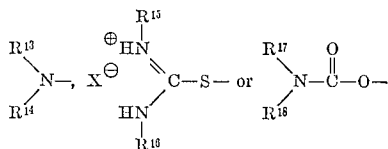
In the above formulas: R, R³, R⁸ and R¹² are each lower alkylene radicals having 1 to 5 carbon atoms including methylene, ethylene, propylene, butylene, isobutylene, and amylene. R¹, R², R⁴, R⁵ and R⁹ are each hydrogen atoms, lower alkyl radicals having 1 to 5 carbon atoms or aryl radicals as described below for R⁶ and R⁷. R⁶ and R⁷ are each aryl radicals such as phenyl and naphthyl, and typically include substituted aryl radicals as illustrated by the radical having the formula



wherein D is typically a nitro radical, a hydroxy radical, a chloro radical, a bromo radical, a lower alkyl radical having 1 to 5 carbon atoms or a lower alkoxy radical wherein the alkyl moiety has 1 to 5 carbon atoms. R¹⁰ and R¹¹ are each cyano radicals, alkoxycarbonyl radicals wherein the alkyl moiety has 1 to 5 carbon atoms or amido radicals,



X is an anion or acid residue such as chloride, bromide, nitrate, trichloroacetate, perchlorate, formate, acetate, aminoacetate or the like. A is a hydroxy radical or a radical having the formula



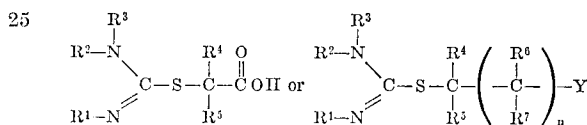
wherein R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷ and R¹⁸ are each hydrogen atoms, lower alkyl radicals having 1 to 5 carbon atoms or an aryl radical as described for R⁶ and R⁷, and X is an anion as described above. M and Z are each hydroxy radicals, carboxy radicals or amino radicals including primary (—NH₂) and secondary amino radicals, and more generally tertiary amino radicals such as morpholino, piperidino, pyrrolidino, and dialkyl amino wherein the alkyl moiety has 1 to 5 carbon atoms. Compounds of Formula C and Formula D above are commonly prepared as salts such as hydrochloride salts to facilitate purifications and to increase their water solubility to facilitate

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incorporation in photographic layers. Suitable compounds within the scope of these generic structures include

- 2-hydroxyethylisothiuronium chloride
- 2-hydroxyethylisothiuronium trichloroacetate
- 5 isothiureidoacetic acid
- 2-isothiureidopropionic acid
- β-(2-morpholinoethylthio)-β-phenylpropionophenone hydrochloride
- 2-ethylaminoethylisothiuronium chloride
- 10 2-hydroxypropylisothiuronium trichloroacetate
- α-Nitrilo-β-(2-morpholinoethylthio) propionitrile hydrochloride
- α-Carbethoxy-β-(2-morpholinoethylthio)-β-phenylpropionitrile hydrochloride
- 15 Ethyl α-amido-β-(2-morpholinoethylthio)-β-phenylpropionate hydrochloride
- 2-hydroxyethyl-1-methylisothiuronium chloride
- 2-hydroxyethyl-1-phenylisothiuronium chloride
- 1-phenyl-2-isothiureidoacetic acid
- 20

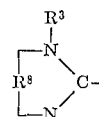
Other suitable stabilizer precursors include those within the scope of the U.S. Pat. 3,220,839—Herz and Kalenda. These include isothiurea derivatives represented by the general structures:



- 25 R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ can be hydrogen atoms, hydrocarbon radicals such as aryl radicals as illustrated by phenyl radicals, alkyl-substituted phenyl and alkyl radicals and substituted alkyl radicals. R¹ and R² can also be acyl radicals having the formula
- 30
- 35



- 40 wherein R is an alkyl radical. R¹ and R² together can be the necessary atoms to form a heterocyclic ring or preferably they can be the necessary carbon and hydrogen atoms to form an alkylene radical linking both adjacent nitrogen atoms to form a cyclic nucleus as illustrated by the following moiety wherein R⁸ is an alkylene radical,
- 45



- 50 wherein R³ can be an acyl radical in addition to those substituents described above for R³. The letter n can be an integer of at least 1, and generally 1 to 10, and preferably 1 to 3. The letter Y can be a carboxyl radical, a sulfonate radical, a hydroxyl radical or an amino radical, including substituted amino radicals, of the formula
- 55



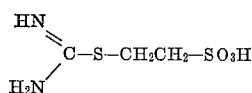
- 60 wherein R⁹ is a hydrogen atom or an alkyl radical, and wherein R¹⁰ is a hydrogen atom, an alkyl radical or an acyl radical, their salts having the formula
- 65



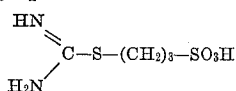
- 70 or a morpholino radical. Typical alkyl and alkylene radicals referred to above have 1 to 20 carbon atoms and more generally 1 to 4 carbon atoms. Illustrative alkyl radicals include methyl, ethyl, isopropyl, n-butyl, 2-ethylhexyl, n-decyl, stearyl, n-eicosyl and the like radicals. Alkylene radicals analogous to such alkyl radicals are
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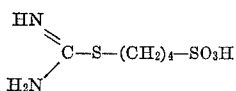
suitable R⁸ substituents. Suitable compounds within the scope of this structure include, for example, 2-S-thiuronium ethane sulfonate:



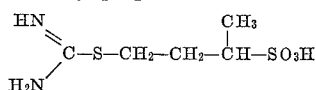
3-S-thiuronium propane sulfonate:



4-S-thiuronium butane sulfonate:



3-S-thiuronium methyl-propane sulfonate



In one embodiment the above compounds which contain a sulfonate radical and form so-called inner acid salts are preferred stabilizer precursors. Inner acid salts as employed herein are defined in U.S. Pat. 3,220,839—Herz and Kalenda.

The stabilizer precursors according to this invention are generally stable and substantially inert in photographic silver halide emulsions in acidic or neutral media and under temperatures that prevail during conventional storage and use of the photographic products. However, the stabilizer precursors can be activated by contact with basic solutions or preferably at elevated temperatures above about 200° F.; the sulfur containing derivatives of the invention are decomposed or transposed to an active form which will stabilize silver halide. Generally, it is desirable to employ temperatures in the range of about 190° F. to 500° F. and preferably from about 200° F. to 400° F. The higher temperatures significantly shorten processing time in most instances to a period of less than about 8 seconds and usually in the range of about 1 to 5 seconds.

Generally, heating according to the invention can be carried out by contacting the photographic element containing the stabilizer precursor with suitable heating means such as metal rolls, infrared radiation, heated plates and the like.

It is usually desirable to effect the required stabilization within as short a time as possible. The duration of the heating step within the desired range will be influenced by such factors as the temperature employed and other addenda present. The optimum heating period can be readily determined considering the temperature, suitable stabilization and other factors which can be determined by those skilled in the art.

In some instances it is also desirable to incorporate a stabilizer activator precursor in the emulsion to aid in decomposition or transposing of the above compounds to an active form. Typical classes of stabilizer activator precursors which can be used include guanidinium salts, such as diguanidinium glutarate, succinate, malonate, adipate, pimelate or itaconate; monoguanidinium malonate, succinate or trichloroacetate and other compounds which decompose when heated to form a free base.

Since certain of the stabilizer precursors can be activated by inorganic alkalis such as alkali metal hydroxides including sodium hydroxide and potassium hydroxide and alkali metal carbonates such as sodium carbonates, it is usually desirable not to contact the elements containing the precursors of the invention before heating and photo-development with alkaline materials which would cause premature stabilization. However, they can be stabilized by contact with alkali materials, if desired, after photo-development.

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The stabilizer precursor and stabilization activator precursor can be incorporated in photographic emulsions or layers of photographic elements by using any of the photographic techniques commonly used in emulsion making. For example, they can be dissolved in a suitable solvent and added as such or they may be added in the form of a dispersion. Techniques which may be employed in adding the precursor combinations to photographic elements can be similar to the techniques used for adding color couplers to photographic emulsions. Techniques of this type are disclosed, for example in U.S. Pat. 2,320,227 and U.S. Pat. 2,801,171. Solvents or diluents which are miscible with components employed may be utilized to aid in the addition.

The silver halide compositions which are generally useful in accordance with this invention comprise silver halide grains having polyvalent metal ions or atoms occluded therein. The silver halide grains having occluded polyvalent metal ions therein are generally obtained by precipitating in the presence of the polyvalent metal ions and preferably in an acid medium. Typical emulsions of this type are disclosed in French Pat. 1,456,581, made available Oct. 28, 1966, and in Bacon, U.S. Ser. No. 629,090 filed Apr. 7, 1967, now pending. These emulsions are useful in recording electromagnetic radiation such as electrons, light, X-rays, etc. In certain preferred embodiments of this invention the emulsion contains silver halide grains with trivalent metal ions occluded therein.

The silver halide compositions of this invention have a halogen acceptor which is generally contiguous with the silver halide grains in the system. Generally, suitable halogen acceptors are compounds which enhance the photolytic yield (as determined by radiographic analysis, for example) and/or the photolytic density of a print-out emulsion.

Generally, the halogen acceptors are nitrogen containing halogen acceptors such as those disclosed in Bacon et al., French Pat. 1,456,581, and preferably they are urazole type halogen acceptors such as disclosed in Bacon et al., French Pat. 1,450,984 issued Aug. 18, 1966. Typical urazole type halogen acceptors include urazole sodium salt, urazole, 3-thiourazole, 3,5-dithiourazole, 3,5-dithiourazole salt, 4-iminourazole hydrazine salt, 4-(1-naphthyl)urazole, 4-ethyl urazole, 1-phenyl urazole, 4-phenyl urazole, 1-butyl urazole, 1-octyl urazole, 4-butyl-3,5-dithiourazole, 1,4-diphenyl urazole, 1,4-dibutyl urazole, 1,4-di-butyl-3,5-dithiourazole, 1,4-diphenyl-3,5-dithiourazole, 1-ethyl-4-phenylurazole, 1-ethyl-4-phenyl-3,5-dithiourazole, 3-thio-5-iminourazole, 3,5-diselenourazole and the like.

In one preferred embodiment of the invention wherein heat is used to activate the stabilizer precursor, a halogen acceptor is utilized which remains effective for enhancing the photolytic yield or photolytic density of a print-out emulsion after having been heated to the activation temperature of the stabilizer precursor. Generally, metal salts and cyclic compounds having an oxo function or thione function (or tautomers thereof) on the ring are suitable in this embodiment. Typical cyclic compounds of this type include the urazole compounds above mentioned.

Various colloids can be used as vehicles or binding agents in preparing the silver halide emulsions of this invention. Satisfactory colloids which can be used for this purpose include any of the hydrophilic colloids generally employed in the photographic field including, for example, gelatin, colloidal albumin, polysaccharides, cellulose derivatives, synthetic resins such as polyvinyl compounds, including polyvinyl alcohol derivatives, acrylamide polymers and the like. In addition to the hydrophilic colloids, the vehicle or binding agent can contain hydrophobic colloids such as dispersed polymerized vinyl compounds, particularly those which increase the dimensional stability of photographic materials. Suitable compounds of this type include water-insoluble polymers of alkyl acrylates or methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

The above-described emulsions of the invention can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include, glass, metals, paper, polyethylene-coated paper, polypropylene-coated paper, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film and related films of resinous materials and others. In one preferred embodiment wherein high temperatures can be used to process the elements of this invention, film supports are utilized which have a heat distortion temperature of at least 160° C. and more preferably of 180° C. in both the length and width directions of the support; heat distortion temperature can be calculated according to ASTM-D-1637-61. Typical preferred supports of this embodiment are heat set polyesters, for example, polyethylene terephthalates, cyclohexylenedimethylene terephthalates and etc.; high temperature polyimides, heat resistant polycarbonates, and related film supports having high heat distortion temperatures.

In one preferred embodiment silver halide emulsions according to the present invention can be utilized as light-developable materials to provide good image records with improved properties, such as high resistance to moisture discoloration, acceptable image background color and high background stability when exposed to light for prolonged periods of time. A suitable light-development process is disclosed in Colt, French Pat. 1,490,026 issued June 19, 1967. In such a photodevelopment application, the silver halide coating is imagewise exposed to form a latent image, the exposed coating heated to at least about 300° F., and after heating the coating is uniformly exposed to light for a time sufficient to produce a visible image. The heating step in such a photodevelopment process represses the usual printing out of unexposed or non-image areas (D_{min}), the original recording sensitivity of the silver halide being inactivated by such heating. Images thus prepared have a high degree of permanence or stability to ambient light.

The invention can be further illustrated by the following examples of 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 unless otherwise specifically indicated.

EXAMPLE 1

A radiation-sensitive gelatino silver bromoiodide (94 mole percent bromide and 6 mole percent iodide) photographic emulsion containing silver halide grains having polyvalent ions occluded therein is prepared and coated as described in Example 19, Emulsion B of Bacon et al., U.S. Ser. No. 625,590 filed Mar. 24, 1967, now Pat. No. 3,447,927, issued June 3, 1969. The coated emulsion is bathed over half of its area (Area 3 and Area 4) in a solution containing 19.8 gr./l. of 3-S-thiuronium propane sulfonate for about 1 minute. After drying, part of the sample is exposed to tungsten light to obtain maximum density (Area 1 and Area 3). The remainder is unexposed (Area 2 and Area 4). The entire sample is heated with the front surface in contact with a Teflon-coated block at 230° C. for 4 seconds. The heated sample is then exposed to daylight fluorescent light (photolyzed) for 15 minutes at 250 footcandles after which the entire sample is soaked in water for 10 seconds. After drying, the sample is photolyzed for an additional 1 hour at 250 footcandles. A control sample of the same emulsion is prebathed in water over a portion of the area prior to exposure and heating.

The respective portions of the sample having the following indicated treatments produced the color appearance indicated (color density is indicated in parenthesis on a seven point scale with 1 being the lightest shade and 7 being the darkest).

	Stabilizer	Tungsten light exposure	Color
Area 1.....	None.....	X(D_{max})....	(7) blue.
Area 2.....	do.....	(D_{min}).....	(3) red.
Area 3.....	X.....	X(D_{max})....	(7) blue.
Area 4.....	X.....	(D_{min}).....	(1) blue.
Control (prebathed).....	None.....	(D_{max}).....	(7) blue.
		(D_{min}).....	(4) red.
Control (not prebathed).....	do.....	(D_{max}).....	(7) blue.
		(D_{min}).....	(2) red.

EXAMPLE 2

A photographic emulsion is prepared and coated as described in Example 1. The stabilizing agents indicated in Table I are used to treat the coated emulsion.

TABLE I

Stabilizer:	Concentration G./l.
2 - hydroxypropylisothiuronium trichloroacetate	29.9
β -Isothiureidopropionic acid	14.8
2-S-thiuronium ethane sulfonate	18.4
3-S-thiuronium 1-methyl propane sulfonate ..	21.2
4-S-thiuronium butane sulfonate	21.2

The samples are heated to 230° C. and photolyzed; no red print-up is produced in the portions of the samples containing stabilizers whereas the unstabilized portions printed up to a high red density of at least 0.5.

Similar results are obtained when the halogen acceptors, urazole, 3-thiourazole, 3,5-dithiourazole, 4-iminourazole hydrazine salt, 3-thio-5-iminourazole, and 1,4-diphenylurazole are used in the above emulsion.

EXAMPLE 3

A silver bromoiodide emulsion is precipitated in the presence of polyvalent metal ions as described in Example 1. To separate samples of the emulsion are added 0, 100 mg., 1 g., 10 g., and 100 g. of 3-S-thiuronium propane sulfonate per mole of silver. The samples are coated and then exposed to tungsten light through a step tablet and heated for 4 seconds at 230° C. They are then photolyzed for 5 minutes at 250 footcandles. A portion of each step is immersed in water for 15 seconds, dried and photolyzed for an additional hour. The results are as follows:

TABLE II

Stabilizer g./mole Ag	Dry area minimum density	Wetted area minimum density
0.....	0.19	0.26
0.1.....	0.18	0.26
1.....	0.18	0.27
10.....	0.19	0.21
100.....	0.20	0.20

Similar results are obtained when the emulsion comprises silver halide grains precipitated in the presence of iridium ions.

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

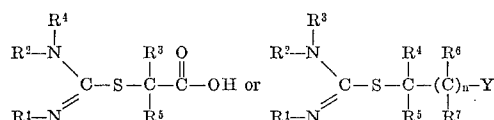
I claim:

1. A silver halide system containing silver halide grains having polyvalent ions occluded therein, said silver halide system comprising a halogen acceptor adjacent said silver halide grains and a stabilizer precursor.

2. A silver halide system according to claim 1 wherein said stabilizer precursor is a thio compound having at least one alkyl group attached to the thio atom.

3. A silver halide system according to claim 1 wherein said stabilizer precursor is a linear sulfur-containing compound.

14. A silver halide system according to claim 1 wherein said stabilizer precursor is in isothioureia derivative having the formula



wherein R³, R⁴, R⁵, R⁶ and R⁷ can be hydrogen atoms, alkyl groups or phenyl groups; R¹ and R² are hydrogen, 40 alkyl, phenyl, acyl having the formula



15. A silver halide system according to claim 14 containing from about .001 to about 1 mole of said stabilizer precursor per mole of said silver halide.

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$$\begin{array}{c} \text{H}_2\text{N} \\ \diagdown \\ \text{C} - \text{S} - (\text{CH}_2)_3 - \text{SO}_3\text{H} \\ \diagup \\ \text{HN} \end{array}$$

18. A process for forming light developed images which comprises imagewise exposing a light-developable, silver halide emulsion to a short duration, high-intensity light of at least 0.1 footcandle-seconds at an intensity of more than about 100 footcandles to form a latent image in said emulsion, heating said emulsion to at least 190° F., and thereafter subjecting the imagewise exposed emulsion to an overall exposure to light of a lower intensity than said imagewise exposure to photodevelop said latent image, said silver halide emulsion comprising (1) silver halide grains having polyvalent metal ions occluded therein, and (2) a halogen acceptor; said process further comprising bathing said emulsion in a stabilizer precursor which has a transition temperature of at least 190° F. before said heating step.

UNITED STATES PATENTS

3,220,839	11/1965	Herz et al. -----	96—61
3,248,219	4/1966	Jacobs -----	96—61 X
3,301,678	1/1967	Humphlett et al. -----	96—61

WILLIAM D. MARTIN, Primary Examiner
P. ATAGUILE, Assistant Examiner

U.S. Cl. X.R.

96—61

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,535,115 Dated October 20, 1970

Inventor(s) Joanne B. Weber

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 21, "siimlar" should read ---similar---.
Column 2, line 25, "yiled of" should read ---yield or---. In
column 3, line 45, following the formula, should be inserted
---.---. In column 6, line 11, following "for example" should be
inserted ---,---. Column 6, that portion of lines 42 thru 44
reading "3,5-dithiourazole salt, 4-iminourazole hydrazine salt,
4-(1-naphthyl-urazole," should read --- 3,5-dithiourazole hydra-
zine salt, 4-iminourazole hydrazine salt, 4-(1-naphthyl)urazole,---.
In column 9, line 31, "in" should read ---an---.

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Commissioner of Patents