United States Patent Office 3,408,197 Patented Oct. 29, 1968

3,408,197

SYNERGISTIC SENSITIZATION OF SILVER HALIDE EMULSIONS WITH LABILE SELENIUM FORMED IN SITU

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No Drawing. Filed Jan. 3, 1967, Ser. No. 606,586
9 Claims. (Cl. 96—108)

ABSTRACT OF THE DISCLOSURE

Sensitizing photographic systems, such as silver halide emulsions, with a noble metal and labile selenium which is formed in situ by activating a non-labile selenium compound, said activating being accomplished by adding said noble metal, heating to sensitize, adding said non-labile selenium compound and further heating to increase the sensitivity.

This invention relates to photography. In one aspect, this invention relates to processes of sensitizing photographic systems.

In the Dunn application Serial No. 468,972 filed July 1, 1965, now U.S. Patent 3,297,446 he found that a sensitizer combination of a noble metal and labile selenium produced a synergistic effect in photographic systems. There are many readily available selenium compounds which are not labile, however, and it would be desirable to employ these compounds in a sensitizing process. This invention provides a way for employing these compounds in such a sensitizing process.

It is an object of this invention to provide a process for sensitizing photographic systems with a noble metal and labile selenium wherein a non-labile selenium compound is employed in the process.

Another object of this invention is to provide a process for sensitizing photographic silver halide emulsions with a noble metal and labile selenium wherein a non-labile selenium compound is employed in the process.

Still another object of this invention is to provide a process for sensitizing photographic systems and more particularly silver halide emulsions with gold and labile selenium wherein a non-labile selenium compound is employed in the process.

Other objects will become apparent hereinafter.

These and other objects of the invention are accomplished by sensitizing photographic systems and more particularly silver halide emulsions with a noble metal and labile selenium which is formed in situ by activating a non-labile selenium compound, said activating being accomplished by adding said noble metal, heating to sensitize, adding said non-labile selenium compound and further heating to increase the sensitivity. It was previously thought that non-labile selenium compounds could not be effectively employed in combination with noble metals in a sensitizing process for photographic systems. I have found, however, that non-labile selenium compounds can be activated by the process of this invention so that they become labile and, in combination with noble metals, give synergistic sensitization. Other methods for activating non-labile selenium compounds to make them labile are disclosed and claimed in my copending application Serial No. 606,588 entitled "Sensitizing Photographic Systems (Case A)" and copending application Serial No. 606,587 entitled "Sensitizing Photographic Systems" of my co-worker Dunn, both filed concurrently herewith.

The term "labile" has a meaning well understood by those skilled in the art of photography and is defined in the Dunn application Serial No. 468,972, U.S. Patent 3,297,446 filed July 1, 1965, as being a material which yields a silver selenide that is insoluble in water at room temperature (20° C.) upon addition to an aqueous silver nitrate solution. Likewise, the term "non-labile" as used herein in describing selenium compounds has a meaning well understood by those skilled in the art of photography, i.e., a material which does not yield a silver selenide that is insoluble in water at room temperature (20° C.) upon addition to an aqueous silver nitrate solution. For example, potassium selenocyanate and selenous acid are non-labile selenium compounds since silver selenide does not precipitate when these compounds are added to an aqueous silver nitrate solution.

Non-labile selenium compounds which can be used in this invention include, for example, potassium selenocyanate, selenous acid, inorganic isoselenocyanate complexes, etc.

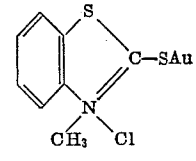
The concentration of the non-labile selenium compound which is activated to form labile selenium in situ can be varied considerably depending upon the particular non-labile selenium compound employed, the nature of the photographic system, the amount and chemical nature of the noble metal sensitizer, etc. In silver halide systems, for example, I have found that useful results can be obtained using amounts as small as 0.05 milligram of non-labile selenium compound per mole of silver halide although considerably larger amounts can also be employed, such as 5.0 milligrams or more per mole of silver halide.

The noble metal sensitizers useful in my invention include the well-known gold sensitizers and other noble metals such as palladium, platinum and any of those disclosed in Smith et al., U.S. Patent No. 2,448,060 issued August 31, 1948. Typical suitable gold sensitizers are described in Waller et al., U.S. Patent No. 2,399,083 issued April 23, 1946, and Damschroder et al., U.S. Patent 2,642,361 issued June 16, 1953.

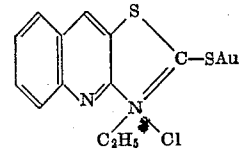
Illustrative addenda suitable for furnishing the noble metal moiety in the sensitizer combinations of the invention include:

Gold chloride,
Potassium aurate,
Potassium auriaurite,
Potassium auricyanide,
Potassium aurithiocyanate,
Gold sulfide,
Gold selenide,
Gold iodide,
Potassium chloroaurate,
Ethylenediamine-bis-gold chloride,
Ammonium chloroplatinite, i.e. $(NH_4)_2PtCl_4$,
Ammonium chloropalladate, i.e., $(NH_4)_2PdCl_6$; and
Organic gold sensitizers having the formulas:

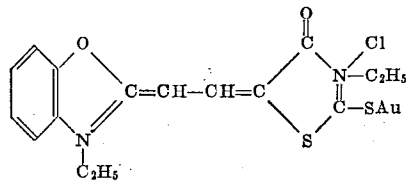
I.



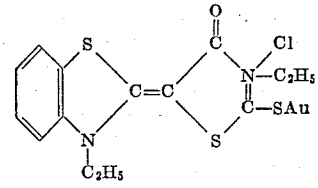
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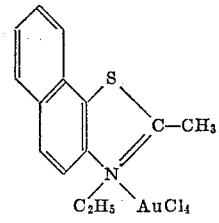
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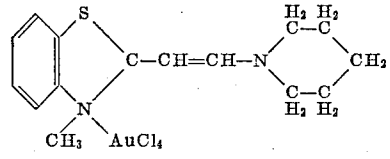
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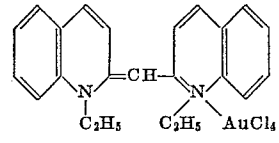
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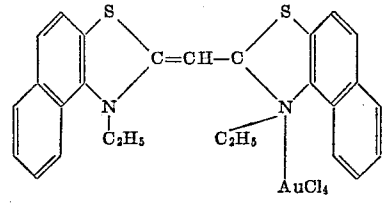
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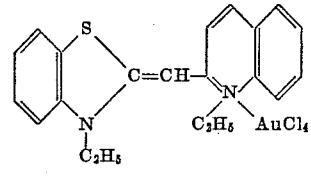
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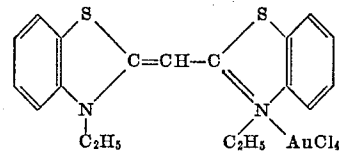
VIII.



IX.



X.



The concentration of noble metal sensitizer useful in my invention can be any amount suitable for the intended purpose. I have found, for example, that amounts varying from about 0.1 to about 10.0 milligrams of gold sensitizer per mole of silver halide are quite satisfactory although higher amounts can also be employed.

In Example 8 of the Dunn application Ser. No. 468,972, now U.S. Patent 3,297,446, it was disclosed that compounds containing a selenius atom which is not labile do not provide the very high increase in speed described therein for combinations including labile selenium compounds. I have found, however, that non-labile selenium compounds can be activated in accordance with the instant invention to convert compounds, in combination with noble metals, perform in the same manner as the labile selenium compounds in the Dunn application and act as a synergistic sensitizer combination to give the very photographic speed disclosed in said previous case.

U.S. Patent 3,243,298, column 68, lines 35–38, and British Patent 861,984, page 2, lines 42–44 disclose the use of potassium selenocyanate as a sensitizer. There is no disclosure of the use of this compound in combination with noble metals, however, or that sensitizing in two steps will activate the potassium selenocyanate to convert it to a labile form so that it will give synergistic sensitizing results in combination with noble metals as set forth in this invention.

The temperature and length of time for the heating steps in my novel sensitizing process can be considerably varied depending upon the particular photographic system, the concentration of the non-labile selenium compound, the concentration of the noble metal compound, etc. Generally, varying each heating step from about 55° C. to about 70° C. for about 20 minutes to about 100 minutes has been found to be satisfactory for silver halide emulsions.

It has been found that particularly useful results are obtained when the sensitizer mixture used in the sensitizing process of the invention contains a water-soluble thiocyanate compound. Typical thiocyanates include sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, etc. The amount of thiocyanate compound used can be varied depending upon the particular system being sensitized, relative amounts of sensitizers employed, etc.

The sensitizing addenda of my invention can be added in a variety of ways to photographic systems and at various stages in the preparation of such. In general, with respect to silver halide emulsions, such addenda can be added with useful effects at the completion of the Ostwald ripening and prior to one or more of the final digestion operations. The sensitizing addenda are preferably added to silver halide emulsions after the silver halide grains are substantially in their final size and shape. The addenda can be added in the form of their aqueous solutions, where they are soluble in water, or in an innocuous organic solvent where the sensitizer does not have sufficient solubility in water to be used in the form of an aqueous solution. Particularly useful organic solvents include ethanol, methanol, pyridine, acetone, dioxane, etc. Organic solvents which have a rather high degree of polarity are preferred. Where it is desired to add the sensitizing addenda in some other form than a solution, this procedure is also possible, especially where the sensitizer is available in the form of a colloidal suspension. In some cases, it is possible to add the sensitizers suspended in an organic solvent which forms very small suspended particles in the photographic emulsion similar to the type of colloidal particle produced in preparing coupler dispersions. Dispersing media useful for this purpose include tricresyl phosphate, dibutyl phthalate, triphenyl phosphate, etc.

Vacuum deposited photographic systems substantially free of conventional vehicles, binders or dispersing agents can also be sensitized in accordance with the invention by incorporating the sensitizers in a coating or layer contiguous to the vacuum deposited light-sensitive material. Suitable vacuum deposited silver halide systems that can be sensitized in accordance with the invention are disclosed in Rasch et al. application U.S. Serial No. 415,596 filed December 3, 1964; Rees application U.S. Serial No. 421,725 filed December 28, 1964; and Belgian Patent 639,020.

The silver halide emulsion of a photographic element which can be sensitized according to this invention can contain conventional addenda such as gelatin plasticizers, coating aids, antifoggants such as the azaindene and hardeners such as aldehyde hardeners, e.g., formaldehyde,

mucochloric acid, glutaraldehyde bis(sodium bisulfite), maleic dialdehyde, aziridines, dioxane derivatives and oxypolysaccharides. The addenda may be added to the emulsion before or after sensitizing dyes, if any, are used. Sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Patents 2,526,632 and 2,503,776. Spectral sensitizers which can be used are the cyanines, merocyanines, complex (trinuclear) cyanines, complex (trinuclear) merocyanines, styryls and hemicyanines. Developing agents can also be incorporated into the silver halide emulsion if desired or can be contained in a separate underlayer. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide.

The silver halide emulsion layer of a photographic element which can be sensitized according to the instant invention can contain any of the hydrophilic water-permeable binding materials suitable for this purpose. Suitable materials include gelatin, colloidal albumin, polyvinyl compounds, cellulose derivatives, acrylamide polymers, etc. Mixtures of these binding agents can also be used. The binding agents for the emulsion layer of the photographic element can also contain dispersed polymerized vinyl compounds. Such compounds are disclosed, for example, in U.S. Patents 3,142,568; 3,193,386; 3,062,-674; and 3,220,844, and include the water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates and the like.

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

I have found that the speed of photographic emulsions sensitized according to the invention can be further increased by including in the emulsions a variety of hydrophilic colloids, such as carboxymethyl protein of the type described in U.S. Patent 3,011,890 issued December 5, 1961, and polysaccharides of the type described in Canadian Patent 635,206.

Photographic emulsions sensitized according to the invention can contain speed increasing compounds such as quaternary ammonium compounds, polyethylene glycols or thioethers. Frequently, useful effects can be obtained by adding the aforementioned speed increasing compounds to the photographic developer solutions instead of, or in addition to, the photographic emulsions.

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

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

The sensitizing process of the invention can be utilized to sensitize any photographic system that can be sensitized with noble metals. The invention thus has utility, not only for silver halide photographic systems, but also, for other light-sensitive systems such as other light-sensitive silver salts, thallous halides, cuprous halides, lead halides and related light-sensitive heavy metal salts.

Photographic elements which have been sensitized according to the process of the instant invention may be stabilized with labile sulfur compounds in accordance with my application Serial No. 486,235 filed September 9, 1965, now U.S. Patent 3,297,447. These labile sulfur compounds provide a particularly efficacious means of controlling fog without deleteriously affecting the speed of the stabilized photographic system. Particularly useful labile sulfur compounds include the water-soluble thiosulfates such as alkali metal thiosulfates including sodium and potassium thiosulfates, as well as ammonium thiosulfate; thioureas such as thiourea, allylisothiourea, diacetyl thiourea; thiosemicarbazide; thiocarbamates such as isopropylthiocarbamate; etc.

The amount of labile sulfur compound used to stabilize photographic systems sensitized by the process of this invention can vary considerably depending upon the particular sensitized photographic system employed, finishing conditions, including temperature and time of digestion and ripening, etc. In silver halide photographic systems particularly useful results have been obtained at concentrations of about 0.1 to 10 milligrams per mole of silver halide. Larger or smaller quantities can be employed without adversely affecting the sensitometric properties of the photographic system. The labile sulfur compounds are efficaciously added to be present during the chemical sensitization of the photographic system.

The following example will illustrate the invention but is not to be construed to limit it in any way.

EXAMPLE

A medium-grain silver bromoiodide emulsion containing 3.4 mole percent iodide is prepared. A first portion of the emulsion is chemically sensitized by the addition of 2 mg. of potassium chloroaurate per silver mole, 50 mg. of sodium thiocyanate per silver mole and 8 mg. of sodium thiosulfate per silver mole. The emulsion is then heated for 10 minutes at 65° C.

A second portion of the emulsion is sensitized with 8 mg. of sodium thiosulfate per silver mole and 50 mg. of sodium thiocyanate per silver mole. The emulsion is then heated for 10 minutes at 60° C. The emulsion is then cooled to 40° C. and 2 mg. of potassium chloroaurate per silver mole and 50 mg. of sodium thiocyanate per silver mole are added. The emulsion is then heated for 5 minutes at 60° C.

A third portion of the emulsion is sensitized with 8 mg. of potassium chloroaurate per silver mole, 100 mg. of sodium thiocyanate per silver mole and 1.2 mg. of potassium selenocyanate per silver mole. The emulsion is then heated for 40 minutes at 70° C.

A fourth portion of the emulsion is sensitized with 8 mg. of potassium chloroaurate per silver mole and 100 mg. of sodium thiocyanate per silver mole. The emulsion is then heated for 40 minutes at 65° C. The emulsion is then cooled to 40° C. and 1.2 mg. of potassium selenocyanate per silver mole are added. The emulsion is then heated for 40 minutes at 65° C.

A fifth portion of the emulsion is sensitized with 2 mg. of potassium chloroaurate per silver mole, 0.8 mg. of N,N-dimethylselenourea per silver mole and 100 mg. of sodium thiocyanate per silver mole. The emulsion is then heated for 10 minutes at 65° C.

A sixth portion of the emulsion is sensitized with 0.8 mg. of N.N-dimethylselenourea per silver mole and 50 mg. of sodium thiocyanate per silver mole. The emulsion is then heated for 3 minutes at 65° C. The emulsion is then cooled to 40° C. and 2 mg. of potassium chloroaurate per silver mole and 50 mg. of sodium thiocyanate per silver mole are added. The emulsion is then heated for 10 minutes at 60° C.

The emulsions are then coated on a cellulose acetate support at a coverage of 540 mg. of silver per square foot. The coatings are then exposed on an intensity scale sensitometer, processed for 5 minutes in Kodak Developer DK–50, fixed, washed and dried.

The following results are obtained:

Portion	Sensitizers	Relative Speed	Fog
First (sensitizers added together).	Sodium thiosulfate plus potassium chloroaurate.	100	0.07
Second (sensitizers added separately).	do	100	0.04
Third (sensitizers added together).	Potassium chloroaurate plus potassium selenocyanate.	100	0.28
Fourth (sensitizers added separately).	do	112	0.22
Fifth (sensitizers added together).	N,N-dimethylselenourea plus potassium chloroaurate.	120	0.18
Sixth (sensitizers added separately).	do	120	0.22

This example shows the increase in sensitivity which is obtained by employing the process of the invention (compare the third portion with the fourth portion). In contrast to the invention, no increase in sensitivity is obtained by adding conventional sulfur-and-gold-sensitizers in two steps (see first and second portions) or by adding labile selenium-and-gold sensitizers in two steps (see fifth and sixth portions).

Although the invention has been described in detail with reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and as defined in the appended claims.

I claim:

1. A process comprising sensitizing photographic silver halide emulsions with a noble metal and labile selenium, said labile selenium being formed in situ by activating a non-labile selenium compound, said activating being accomplished by

(a) adding said noble metal to said photographic system,

(b) heating to sensitize said system,

(c) adding said non-labile selenium compound, and

(d) further heating said system to increase the sensitivity of said system.

2. The process of claim **1** wherein said noble metal is gold.

3. The process of claim **1** wherein said non-labile selenium compound is either potassium selenocyanate or selenous acid.

4. The process of claim **2** wherein said non-labile selenium compound is either potassium selenocyanate or selenous acid.

5. The process of claim **1** wherein said sensitizing is carried out in the presence of a water-soluble thiocyanate compound.

6. The process of claim **4** wherein said sensitizing is carried out in the presence of a water-soluble thiocyanate compound.

7. The process of claim **1** wherein said silver halide emulsion is stabilized with a labile sulfur compound.

8. The process of claim **4** wherein said silver halide emulsion is stabilized with a labile sulfur compound.

9. The process of claim **6** wherein said silver halide emulsion is stabilized with a labile sulfur compound.

References Cited

UNITED STATES PATENTS

3,297,446	1/1967	Dunn	96—107
3,297,447	1/1967	McVeigh	96—107 X

NORMAN G. TORCHIN, *Primary Examiner.*

R. E. FICHTER, *Assistant Examiner.*

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,408,197 Dated October 29, 1968

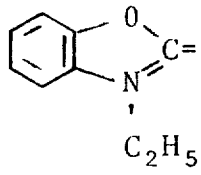
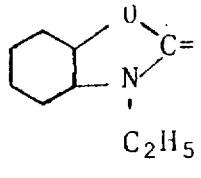
Inventor(s) Patricia A. McVeigh

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

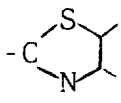
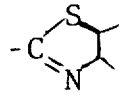
In the Specification

In column 2, columnar line 3, after "468,972," should be inserted --filed July 1, 1965, now--; in columnar line 4, after "3,297,446", delete "filed July 1, 1965".

In column 3, formula III, extreme left portion of for reading

"  " should be --  --; formula VIII,

the right central portion of the formula reading

"  " should be --  ---.

In column 4, columnar line 1, after "convert" should inserted --the selenium to a labile state. After activation, these--; in columnar line 5, after "very" should be inserted --high--.

In column 6, columnar line 69, "N.N-dimethylseleno-urea" should be --N,N-dimethylselenourea--.

SIGNED AND
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(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR
Commissioner of Patents