

1

3,408,196

SENSITIZATION OF SILVER HALIDE EMULSION WITH LABILE SELENIUM FORMED IN SITU

Patricia A. McVeigh, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Jan. 3, 1967, Ser. No. 606,588
13 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 employing a high concentration of noble metal.

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.

Yet still another object of the invention is to provide a sensitizing process for photographic systems which can be easily controlled.

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 employing a high concentration of noble metal. 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.

A unique feature of using the sensitizing process of this invention is that sensitization of photographic systems can be easily controlled. The degree of sensitization can be controlled by varying the concentration of noble metal. A predetermined sensitivity of a photographic system can thus be obtained with the sensitizing process of this invention.

Other methods for activating non-labile selenium com-

2

pounds to make them labile are disclosed and claimed in my copending application Serial No. 606,586 entitled "Sensitizing Photographic Systems (Case B)" 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, filed July 1, 1965, now U.S. Patent 3,297,446, 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.

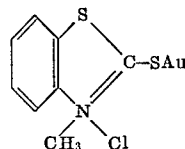
Non-labile selenium compounds which can be used in this invention include, for example, potassium selenocyanate, selenous acid, inorganic isoselenocyanate complexes, etc.

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.

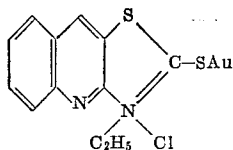
Illustrative addenda suitable for furnishing the noble metal moiety in the sensitizer combinations of the invention include:

Gold chloride,
Potassium aurate,
Potassium auraurite,
Potassium auricyanide,
Potassium aurithiocyanate,
Gold sulfide,
Gold selenide,
Gold iodide,
Potassium chloroaurate,
Ethylenediamine-bis-gold chloride,
Ammonium chloroplatinite, i.e. $(\text{NH}_4)_2\text{PtCl}_4$,
Ammonium chloropalladate, i.e. $(\text{NH}_4)_2\text{PdCl}_6$; and
Organic gold sensitizers having the formulas:

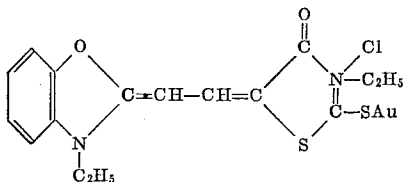


3

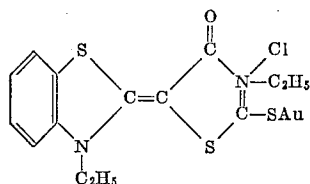
II.



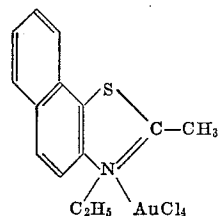
III.



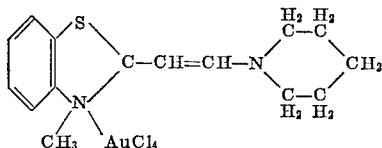
IV.



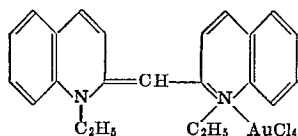
V.



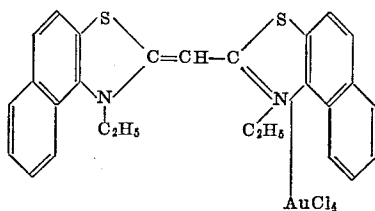
VI.



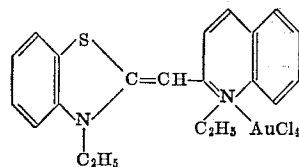
VII.



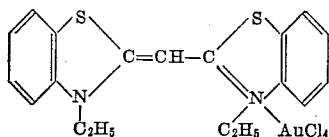
VIII.



IX.



X.



The concentration of noble metal sensitizer useful in my invention to activate the non-labile selenium compound should be at least about 2 moles of noble metal compound per mole of non-labile selenium compound. Preferably, the noble metal sensitizer should be employed in a concentration of from about 4.5 to about 10 moles

4

per mole of non-labile selenium compound, although concentrations of up to 15 moles per mole of non-labile selenium compound can also be employed. If the concentration of noble metal sensitizer is less than about 2 moles per mole of non-labile selenium compound, the non-labile selenium compound will not be sufficiently activated to produce a synergistic sensitizing effect.

In Example 8 of the Dunn application Serial No. 468,972, it was disclosed that compounds containing a selenium 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 the selenium to a labile state. After activation, these 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 high photographic speed disclosed in said Dunn application.

U.S. Patent No. 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 a high concentration of the noble metal 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.

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 Dec. 3, 1964; Rees application, U.S. Serial No. 421,725 filed Dec. 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 oxy-polysaccharides. 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, sulfo-alkyl 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 Dec. 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 non-optically sensitized systems, they can also be used in orthochromatic, panchromatic, and infrared sensitive systems. The sensitizing addenda can be added to photographic systems before or after any sensitizing dyes which are used.

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 Jan. 4, 1955; in silver dye-bleach systems; and emulsions of the mixed-grain type, such as de-

scribed in Carroll and Hanson U.S. Patent 2,592,243, issued Apr. 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 Ser. No. 486,235, filed Sept. 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, allylthiourea, 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 small 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 examples will illustrate the invention but are not to be construed to limit it in any way.

EXAMPLE 1

Test for labile and non-labile selenium compounds

To 10 ml. of distilled water in a test tube are added 6 mg. of potassium selenocyanate. To this solution approximately 5 ml. of 0.1 N silver nitrate are added. No silver selenide is formed which indicates that potassium selenocyanate is a non-labile selenium compound.

To 10 ml. of distilled water in a test tube are added 6 mg. of potassium selenocyanate. When 1.0 ml. of a 10 mg. per ml. solution of potassium chloroaurate is added to 1.0 ml. of the potassium selenocyanate solution the solution turns red. To this red solution approximately 5 ml. of 0.1 N silver nitrate is added. A black precipitate (silver selenide) immediately forms and the supernatant liquid is colorless. This indicates that the potassium selenocyanate becomes labile in the presence of a high concentration of a gold sensitizer.

EXAMPLE 2

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 24 mg. of potassium chloroaurate per silver mole, 100 mg. of sodium thiocyanate per silver mole and 8 mg. of sodium thiosulfate per silver mole. The emulsion is then heated for one minute at 70° C.

A third portion of the emulsion is sensitized with 2 mg. of potassium chloroaurate per silver mole, 100 mg. of sodium thiocyanate per silver mole and 0.8 mg. of N,N-dimethylselenourea per silver mole. The emulsion is then heated for 20 minutes at 65° C.

A fourth portion of the emulsion is sensitized with 100 mg. of sodium thiocyanate per silver mole and 1.6 mg. of potassium selenocyanate per silver mole. The emulsion is then heated for 30 minutes at 60° C.

A fifth portion of the emulsion is sensitized with 2 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.

A sixth portion of the emulsion is sensitized with 24 mg. of potassium chloroaurate per silver mole and 100 mg. of sodium thiocyanate per silver mole. The emulsion is then heated for 20 minutes at 65° C.

A seventh portion of the emulsion is sensitized with 24 mg. of potassium chloroaurate per silver mole, 100 mg. of sodium thiocyanate per silver mole and 0.4 mg. of N,N-dimethylselenourea. The emulsion is then heated for 5 minutes at 60° C.

An eighth portion of the emulsion is sensitized with 6 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 ninth portion of the emulsion is sensitized with 24 mg. of potassium chloroaurate per silver mole, 100 mg. of sodium thiocyanate per silver mole and 1.8 mg. of potassium selenocyanate per silver mole. The emulsion is then heated for 25 minutes at 65° C.

A tenth portion of the emulsion is sensitized with 32 mg. of potassium chloroaurate per silver mole, 100 mg. of sodium thiocyanate per silver mole and 1.8 mg. of potassium selenocyanate per silver mole. The emulsion is then heated for 20 minutes at 65° C.

An eleventh portion of the emulsion is sensitized with 24 mg. of potassium chloroaurate per silver mole, 100 mg. of sodium thiocyanate per silver mole and 0.8 mg. of potassium selenocyanate per silver mole. The emulsion is then heated for 40 minutes at 65° 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	Sensitizer (mg./Ag mole)	Ratio of moles of Au cmpd./mole of S or Se cmpd.	Relative Speed	Fog	Gamma
First (Conventional S and Au sensitizers).....	Sodium thiosulfate (8) plus potassium chloroaurate (2).	0.15	100	0.10	2.96
Second.....	Sodium thiosulfate (8) plus potassium chloroaurate (24).	1.8	68	0.26	3.3
Third (Labile Se and Au sensitizers).....	N,N-dimethylselenourea (.8) plus potassium chloroaurate (2).	0.9	145	0.34	2.98
Fourth.....	Potassium selenocyanate (1.6).....	<1	0.02	-----	-----
Fifth.....	Potassium chloroaurate (2).....	32	0.02	2.00	-----
Sixth.....	Potassium chloroaurate (24).....	100	0.55	2.00	-----
Seventh.....	N,N-dimethylselenourea (0.4) plus potassium chloroaurate (24).	21.9	120	0.90	2.4
Eighth.....	Potassium selenocyanate (1.2) plus potassium chloroaurate (6).	1.7	115	0.26	3.20
Ninth.....	Potassium selenocyanate (1.8) plus potassium chloroaurate (24).	4.64	126	0.52	2.78
Tenth.....	Potassium selenocyanate (1.8) plus potassium chloroaurate (32).	6.18	135	0.53	2.76
Eleventh.....	Potassium selenocyanate (0.8) plus potassium chloroaurate (24).	10.15	138	0.51	2.60

This example illustrates that a high level of gold sensitizer in a conventional sulfur-and-gold sensitized photographic system lowers the speed (compare second portion with the first portion). The above example also shows that increasing the concentration of the gold sensitizer in a gold and labile selenium sensitizing mixture lowers the γ and increases the fog (compare seventh portion with the third portion). The above example also illustrates that sensitizing with gold alone at a high level gives a speed equal to a sulfur-and-gold-sensitized photographic system but lowers the γ and increases the fog (compare sixth portion with the first portion).

The above example also illustrates that when the ratio of the moles of noble metal compound per mole of non-

labile selenium compound is greater than about 2, the non-labile selenium compound becomes activated and functions as a synergistic sensitizing combination with the noble metal to provide a higher speed than conventional sulfur and gold sensitizers (compare eighth, ninth, tenth and eleventh portions with the first portion).

EXAMPLE 3

A coarse-grain silver bromoiodide emulsion containing 2.85 mole percent iodide is prepared. A first portion of the emulsion is sensitized by the addition of 0.6 mg. of potassium chloroaurate per silver mole, 45 mg. of sodium thiocyanate per silver mole and 4 mg. of sodium thiosulfate per silver mole. The emulsion is then heated for 16 minutes at 60° C.

A second portion of the emulsion is sensitized with 4 mg. of gold (I) sulfide per silver mole, 15 mg. of sodium thiocyanate per silver mole and 2.3 mg. of potassium selenocyanate per silver mole. The emulsion is then heated for 30 minutes at 65° C.

A third portion of the emulsion is sensitized with 2 mg. of gold (I) sulfide per silver mole, 15 mg. of sodium thiocyanate per silver mole and 0.34 mg. of potassium selenocyanate per silver mole. The emulsion is then heated for 80 minutes at 65° C.

The emulsions are then coated on a cellulose acetate support at a coverage of 484 mg. of silver per square foot. The coatings are then exposed on an intensity scale sensitometer, processed for 3 minutes in an Elon-hydroquinone developer, fixed, washed and dried. The following results are obtained:

Portion	Sensitizer (mg./Ag mole)	Ratio of moles of Au cmpd./mole of S or Se cmpd.	Relative speed	Fog
First (Conventional S and Au sensitizers).....	Sodium thiosulfate (4) plus potassium chloroaurate (0.6).	0.09	100	0.10
Second.....	Gold (I) sulfide (4) plus potassium selenocyanate (2.3).	0.60	102	0.08
Third.....	Gold (I) sulfide (2) plus potassium selenocyanate (0.34).	2.00	132	0.20

The above example illustrates the synergistic sensitizing effect obtained by employing the sensitizing process of the invention where about 2 moles of a noble metal compound per mole of a non-labile selenium compound are employed. Concentrations of noble metal compounds below this amount do not sufficiently activate the non-labile selenium compound to produce a synergistic sensitizing effect.

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 emulsion 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 employing at least about 2 moles of a noble metal compound per mole of said non-labile selenium compound.

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.

10. The process of claim 1 wherein said noble metal compound is employed in a concentration of from about 4.5 to about 10 moles per mole of said non-labile selenium compound.

11. The process of claim 4 wherein said noble metal compound is employed in a concentration of from about 4.5 to about 10 moles per mole of said non-labile selenium compound.

12. The process of claim 6 wherein said noble metal compound is employed in a concentration of from about 4.5 to about 10 moles per mole of said non-labile selenium compound.

13. The process of claim 9 wherein said noble metal compound is employed in a concentration of from about 4.5 to about 10 moles per mole of said non-labile selenium compound.

References Cited

UNITED STATES PATENTS

3,297,446	1/1967	Dunn	96—107
3,297,447	1/1967	McVeigh	96—109

25 NORMAN G. TORCHIN, *Primary Examiner*.
R. E. FICHTER, *Assistant Examiner*.