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[54] PHOTOGRAPHIC ELEMENTS AND COMPOSITIONS

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[58] Field of Search.....96/66 R, 66 T, 95, 87

[56] References Cited

UNITED STATES PATENTS

2,688,548	9/1954	Reynolds	96/66
2,688,549	9/1954	James et al.	96/66
3,005,710	10/1961	Levy	96/66 X
3,041,170	6/1962	Haist et al.	96/66
3,178,282	4/1965	Luckey et al.	96/66 X
3,220,846	11/1965	Tinker et al.	96/91

2,410,644	11/1946	Fierke et al.	96/95 X
3,159,676	12/1964	Spickett et al.	260/343.7 X
3,438,776	4/1969	Yudelson	96/28

OTHER PUBLICATIONS

Guttman; David E. et al., Chemical Abstracts, 30- Pharmaceuticals, 1964, Col. 374.

Maruha, Juro et al., Chemical Abstracts, Vol. 62, 1965, Col. 3964.

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[57]

ABSTRACT

A thermolabile photographic developing agent precursor which is a reaction product of an acidic silver halide developing agent, such as ascorbic acid or a hydroxy tetronic acid, with a labile organic base, such as urea, an amide or guanidine, is useful in photographic elements and/or compositions in dry processing. These developing agent precursors are activated by heat and/or alkali.

5 Claims, No Drawings

PHOTOGRAPHIC ELEMENTS AND COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to developing agent precursors and to photographic systems containing such precursors. In one of its aspects, this invention relates to photographic elements, compositions and processes, especially dry processes, employing developing agent precursors which are activated by heat and/or alkali. These developing agent precursors are produced by the reaction of an acidic developing agent, such as ascorbic acid, with a labile organic base, e.g., a nitrogen base, such as urea or guanidine.

2. Description of the Prior Art

In the usual process of photographic development, an exposed photographic element comprising a support having at least one photographic silver halide layer, is immersed in a developing bath containing a silver halide developing agent. Developing baths of the prior art normally contain a developing agent, a preservative, such as sodium sulfite, a development activator, such as alkali, to activate the developing agent, and can also contain other materials, such as sodium bromide as a restrainer, antifoggants, etc.

Incorporation of silver halide developing agents in layers of photographic elements is also known. These are developed after light exposure, typically by treating them in alkaline solutions which may or may not contain a developing agent. Following development, the developed silver image can be fixed, washed and dried.

The processes employed to develop these emulsions have been referred to as "wet" processes. Such processes are described, for example, in Mees, "The Theory of the Photographic Process," 3rd Edition (1966) Pages 278-311.

The use of light-sensitive silver halide emulsion layers which contain a developing agent and in which the latent image may be developed by heat processing are also known. These materials usually have the advantage of being processed simply and rapidly without the use of solutions. Such processes have been referred to as "dry" processes, since no liquid processing solutions are required in the development of the photographic image. One process of this type employs the reaction product of an alkaline developing agent, such as p-aminophenol with a readily decarboxylated organic acid. This reaction product is in a photographic element, and the free base developing agent is produced upon heating to decarboxylation temperature as described in U.S. Pat. No. 3,220,846 of Tinker and Sagura, issued Nov. 30, 1965.

Acidic materials such as ascorbic acid, gallic acid and the like have been employed as photographic silver halide developing agents. However, the employment of such acids as silver halide developing agents in photographic coatings such as silver halide emulsions can result in unstable photographic elements that in many cases can not be suitably stored and lose desired sensitometric properties.

There has accordingly been a continuing need for components, especially developing agent precursors, that can be employed in photographic coatings and be easily activated to provide an acidic developing agent when desired, have substantial stability under conditions of storage and usage without causing undesired sensitometric properties.

It is, accordingly, an object of the present invention to provide improved photographic elements, compositions and processes employing developing agent precursors which are reaction products of acidic developing agents with labile organic nitrogen bases providing desired sensitometric properties and storage stability.

Another object is to provide photographic emulsions containing improved developing agent precursors which are reaction products of acidic developing agents and labile organic nitrogen bases.

SUMMARY OF THE INVENTION

In accordance with the invention, a stable, thermolabile photographic developing agent precursor, suitable for incorporation into photographic elements, which is the reaction product of

(A) an acidic silver halide developing agent, especially (a) an ascorbic acid and/or hydroxytetronic acid developing agent, and/or (b) a polyhydroxybenzene developing agent containing a carboxyl and/or sulfonic acid group, with

(B) a labile organic base, such as urea, an amide or guanidine, provides improved stability, desired sensitometric properties, and is especially suitable in dry processing. The developing agent precursors of the invention are normally utilized in photographic elements contiguous to a photographic silver salt for image development by treatment of the photographic element with heat and/or alkali, e.g., ammonia fumes. The photographic elements of the invention containing the developing agent precursors are suitable for dry processing as well as wet processing.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A wide range of thermolabile developing agent precursors can be employed in the practice of the invention. These thermolabile developing agent precursors can be prepared by reacting an acidic silver halide developing agent with a thermolabile organic base. For example, the acidic silver halide developing agent is dissolved in a suitable solvent, such as water or an alcohol, including methanol, ethanol, ethylene glycol, ethyl acetate, or mixtures thereof and the labile organic base, which can, but need not, be in solution is mixed with the corresponding acidic silver halide developing agent composition. The reactants are typically mixed in stoichiometric concentrations, but concentrations outside these can be employed if desired. The resulting mixture is stirred, typically under ambient conditions of temperature and pressure and then allowed to stand until reaction completion, such as about 30 minutes to an hour or more. Typically the resulting reaction product is a semisolid precipitate. This can be separated or recovered employing common methods of separation, e.g., filtration and recrystallization. For example, the precipitate can be filtered and washed with ethyl acetate or other suitable organic solvent.

The described reaction mixture can be heated if desired, e.g., to a temperature of about 50° C. to about 100° C., but the temperature is normally maintained below that at which the labile organic base is evolved from the reaction mixture.

The exact nature of the described reaction product is not fully understood. It is believed that the resulting product is an addition product or a complex.

Normally, the described thermolabile photographic developing agent precursors are prepared in a composition suitable for preparation of a layer of an element, typically a photographic element.

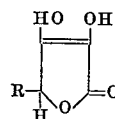
Accordingly, the described reaction product of an acidic silver halide developing agent with a labile organic base can be prepared in situ in a silver halide photographic emulsion if desired. The thermolabile photographic developing agent precursors are normally not recovered.

The thermolabile photographic developing agent precursors employed in the practice of the invention can be prepared employing a wide range of acidic silver halide developing agents. Suitable acidic silver halide developing agents include:

A. 3,4-dihydroxy furan developing agents including ascorbic acid; and/or

B. hydroxytetronic acid developing agents of the formula:

(I)

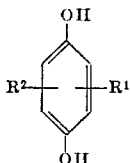


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wherein R is aryl containing up to 20 carbon atoms, e.g., six to 20 carbon atoms, such as, phenyl, tolyl or naphthyl, or the group $Z-CH_2-(CHOH)_{n-1}$, wherein n is 1 to 4, Z is hydroxy when n is 1 and hydrogen or hydroxyl when n is 2 to 4; and/or

C. phenolic developing agents of the formula:

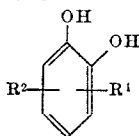
(II)



wherein R^1 and R^2 are the same or different, and each is carboxy, i.e., $-COOH$, a sulfonic acid group, e.g., $-SO_3H$, hydrogen, hydroxyl, halogen, e.g., chlorine, bromine or iodine, or alkyl containing one to five carbon atoms, i.e., methyl, ethyl, propyl, butyl and pentyl; wherein at least one of R_1 and R_2 is carboxy or a sulfonic acid group;

D. phenolic developing agents of the formula:

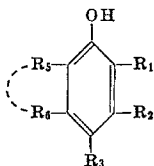
(III)



wherein R^1 and R^2 are as described; wherein at least one of R_1 and R_2 is carboxy or a sulfonic acid group; and/or

E. phenolic developing agents of the formula:

(IV)



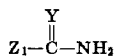
wherein R_1 , R_2 , R_3 , R_4 and R_5 are the same or different, and each is hydrogen, hydroxy, carboxy, a sulfonic acid group, or an amino group, i.e., $-NH_2$, $-NHR_6$ or



is alkyl containing one to five carbon atoms, as described; wherein at least one of the groups R_1 to R_5 is a carboxy group or a sulfonic acid group and at least one of the groups R_1 to R_5 is a hydroxy group or amino group, as described, and R_4 and R_5 when taken together with the aromatic ring to which they are attached can form a naphthalene compound as noted by the broken line in Formula IV.

A wide range of labile organic bases, especially labile organic nitrogen bases, can be employed in preparing the thermolabile developing agent precursors employed in the practice of the invention. These are preferably amide compounds of the formula:

(V)



wherein Y is N, SH, H, or O and wherein Z_1 is hydrogen, alkyl containing one to five carbon atoms, as described, or amino as described.

Suitable labile organic bases include, for example, urea, formamide, acetamide, isobutyramide, guanidine and N-methylurea.

Useful thermolabile photographic developing agent precursors employed in the practice of the invention include, for example, the reaction products of:

guanidine with ascorbic acid,
urea with ascorbic acid,
urea with 1-amino-2-hydroxynaphthalene-6-sulfonic acid,

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urea with 1-amino-2-hydroxynaphthalene-3,6-disulfonic acid,

urea with 3,4,5-trihydroxybenzoic acid,

urea with 2,5-dihydroxybenzoic acid,

formamide with ascorbic acid,

formamide with 1-amino-2-hydroxynaphthalene-6-sulfonic acid,

formamide with 2,5-dihydroxybenzoic acid,

acetamide with ascorbic acid,

acetamide with 1-amino-2-hydroxynaphthalene-6-sulfonic acid,

acetamide with 2,5-dihydroxybenzenesulfonic acid,

acetamide with 3,4,5-trihydroxybenzenesulfonic acid,

N-methylurea with ascorbic acid,

N-methylurea with 1-amino-2-hydroxynaphthalene-6-sulfonic acid,

N-methylurea with 2,5-dihydroxybenzoic acid,

N-methylurea with 3,4,5-trihydroxybenzenesulfonic acid, and the like.

The described thermolabile photographic developing agent precursors can be employed in any suitable location in a photographic system. They are typically employed in one or more layers of a photographic element. Accordingly, one embodiment of the invention comprises an element comprising a support and a thermolabile photographic developing agent precursor which is the reaction product of an acidic silver halide developing agent with a labile organic base.

The described developing agent precursor can be employed in various layers of an element, e.g., in a photographic silver salt emulsion layer, an overcoat layer, a layer under the emulsion layer, a baryta layer, an antihalation layer or any layer which provides the desired developing action upon the heating of the developing agent precursor.

According to this embodiment, an element, especially a photographic element, can comprise a support and a thermolabile photographic developing agent precursor which is the reaction product of ascorbic acid with urea, an amide, as described, or guanidine.

If desired, the described thermolabile photographic developing agent precursors can be employed in a photographic composition, such as a photographic emulsion. A further embodiment of the invention accordingly comprises a photographic composition comprising a photographic silver salt and a thermolabile photographic developing agent precursor which is the reaction product of an acidic silver halide developing agent with a labile organic base.

The described developing agent precursors employed in the practice of the invention can be used in a wide range of photographic emulsions. These are useful in developing and/or incorporation in X-ray or other nonspectrally sensitized emulsions, or with orthochromatic, panchromatic, infrared and other emulsions. They can also be employed with or in photographic emulsions containing spectral sensitizing dyes, such as described in U.S. Pat. Nos. 2,526,632 of Brooker and White issued Oct. 24, 1950 and U.S. Pat. No. 2,503,776 of Sprague issued Apr. 11, 1950. Spectral sensitizers which can be used include cyanines, merocyanines, styryls and hemicyanines.

Various photographic salts, especially photographic silver salts, can be used in the practice of the invention. These include photographic silver halides, such as silver iodide, silver bromide, silver chloride, as well as mixed halides, such as silver bromiodide, silver chloriodide, and the like.

The described developing agent precursors can be incorporated in photographic emulsions or layers of photographic elements using well-known techniques in the photographic art. For example, they can be dissolved in a suitable solvent and added as such or they can be added in the form of a dispersion. Techniques of this type are described, for example, in U.S. Pat. No. 2,322,027 of Jelley et al. issued June 15, 1943; and U.S. Pat. No. 2,801,171 of Fierke et al. issued July 30, 1957.

Coatings, especially photographic coatings, employed in the practice of the invention, are suitable on a wide variety of sup-

ports. Suitable supports include those generally employed for photographic elements, such as various films including cellulose acetate films, cellulose nitrate films, polyethylene terephthalate films, or other polyester films, polycarbonate films and related films or resinous materials; as well as papers, such as paper supports coated with resinous materials, e.g., coated with polyethylene, polypropylene and/or ethylene-butene copolymers; glass; metal, and the like. The supports or layers coated on them can contain fluorescent brightening agents, such as stilbenes, benzothiazoles and benzoxazoles.

The photographic elements according to the invention typically contain one or more layers comprising any of the known binding materials suitable for photographic purposes. These include natural and synthetic binding materials generally employed for this purpose, for example, gelatin, colloidal albumin, water-soluble vinyl polymers, such as mono- and polysaccharides, cellulose derivatives, proteins, water-soluble polyacrylamides, polyvinylpyrrolidone, and the like, as well as mixtures of such binding agents. These binding materials can also contain water-insoluble polymers, such as vinyl polymers, including polymers of acrylates and methacrylates. The elements can also contain stripping layers and/or antistatic layers.

Photographic emulsions employed in the practice of the invention can be chemically sensitized using any of the known procedures employed in emulsion making, such as by digesting with natural active gelatin or various sulfur, selenium, noble metal and/or gold compounds, and/or with reducing agents, such as stannous salts, polyamines and the like.

The developing agent precursors of the invention can be employed in combination with any silver halide developing agent. These can be employed as the main developing agent, or as an auxiliary developing agent. Suitable silver halide developing agents which can be employed in the practice of the invention include, for example, polyhydroxybenzenes, such as hydroquinone developing agents, e.g., hydroquinone, alkyl substituted hydroquinones such as tertiary butyl hydroquinone, methylhydroquinone and 2,5-dimethylhydroquinone; catechol and pyrogallol; chloro substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy substituted hydroquinones, such as methoxyhydroquinone or ethoxyhydroquinone; aminophenol developing agents such as 2,4-diaminophenols, e.g., 2,4-diamino-6-methylphenol, and methylaminophenols; hydroxylamines, such as N,N-di(2-ethoxyethyl)amine; 3-pyrazolidone developing agents, such as 1-phenyl-3-pyrazolidone, including those described in British Pat. No. 930,572; and acyl derivatives of phenols, such as described in British Pat. No. 1,045,303. Such developing agents can be used alone or in combination when employed with the described developing agent precursors.

The described developing agent precursors are typically employed in one or more layers of a photographic element which, after exposure, is treated with a suitable activator, e.g., heat and/or alkali. This is normally carried out by treatment of the photographic element by heating or by contact with ammonia fumes and/or heat. Development according to the practice of the invention can be carried out in the presence or absence of alkali and/or alkali-generating materials. Accordingly, a photographic element of the invention is highly suitable for use in a dry processing system. It may, however, be employed in so-called wet processing systems where the described photographic element is contacted with a suitable activator, such as an aqueous alkaline solution, such as an alkaline solution of an alkali metal hydroxide or carbonate.

Accordingly, another embodiment of the invention comprises a method of developing a latent image in a photographic element comprising a support, an exposed photographic silver salt and a thermolabile developing agent precursor which is the reaction product of an acidic silver halide developing agent with a labile organic base comprising heating the element to a temperature at which the organic base of the developing agent precursor is liberated from the developing agent precursor.

The described developing agent precursors are stable and substantially inert in photographic elements at temperatures which prevail during conventional storage and use of photographic products. However, at temperatures above about 90° C., preferably above about 150° C., e.g., about 150° C. to about 250° C., the acidic developing agent precursors release the described labile organic base to effect development of the exposed areas of the photographic silver salt.

Heating according to the invention can be carried out employing any suitable heating means, such as by contacting the photographic element with heated rollers or plates, infrared lamps or other heating means.

The time for developing a desired image can vary depending on several factors, such as the desired image, the particular components of the photographic element, the specific developing agent precursor employed in the practice of the invention and the like. Generally, however, heating a photographic element according to the invention for about 1 second to about a minute or more is suitable.

It can be advantageous in some cases to employ an antifogant in the practice of the invention such as in the photographic elements described. Suitable antifoggants include organic antifoggants, such as benzotriazole, benzimidazole, 2-mercaptobenzimidazole, and mercaptoazole antifoggants. An inorganic antifogant, such as potassium bromide, potassium iodide and/or sodium bromide, can be employed if desired. A suitable concentration of antifogant can vary depending on the factors described, but usually a concentration of less than about 2 percent by weight of antifogant, e.g., 0.01 to 2 percent by weight is suitable.

When the described developing agent precursors are employed in photographic elements, they can be employed in a wide range of concentrations. Normally, concentrations of about 0.25 to about 4.0 moles of developing agent precursor per mole of silver present in the photographic element is suitable.

Other heat-activatable developers can be employed in the practice of the invention in the described photographic elements and compositions. For example, a heat-activatable developer can be prepared by reacting a para-methylaminophenol developing agent with a sulfite or bisulfite compound, such as sodium sulfite and/or sodium bisulfite, to form a reaction product. These reaction products are useful in photographic elements and/or compositions for dry processing.

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

EXAMPLE 1

This example illustrates preparation of a developing agent precursor of the invention.

Six grams of urea is dissolved in 25 milliliters of distilled water and the resulting solution added slowly with constant stirring to an aqueous ascorbic acid solution containing 17.6 grams of ascorbic acid in 100 milliliters of distilled water. The water is removed from the urea-ascorbic acid solution by means of a rotary evaporator. A white semisolid material is obtained which is the desired reaction product.

EXAMPLE 2

This example illustrates preparation of a photographic element according to the invention.

A paper support containing a baryta coating is coated with a layer 0.004 inches thick of the following composition:

Gelatin (aqueous solution containing 5% by weight gelatin)	40.0 ml.
Silver chloride emulsion (containing 124 g. gelatin and 1 mole of silver in each 2.5 kilograms of emulsion)	2.3 ml.
Ascorbic acid-urea reaction product (as prepared in Example 1)	2.36 g.

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The resulting photographic coating is dried, using forced warm air at a temperature of about 25° C.

EXAMPLE 3

This example illustrates processing an exposed photographic element according to the invention.

A strip of the photographic element prepared as described in Example 2 is sensitometrically exposed. The resulting latent image is developed, employing a dry process by contacting the side of the photographic element opposite the photographic coating with a heated block at a temperature of about 160° C. for a period of 30 seconds. A brown image is obtained.

EXAMPLE 4

This is a comparative example.

A photographic element is prepared as described in Example 2, with the exception that 1.76 grams of ascorbic acid is employed in place of the ascorbic-acid-urea reaction product. A strip of the resulting photographic element is sensitometrically exposed and dry processed in the same manner described in Example 3. A faint brown image is obtained which is barely discernible and unsatisfactory for use compared with the image produced in Example 3.

The presence of ascorbic acid alone produces a photographic coating which is unstable to light and increases the difficulty of stabilizing the undeveloped silver salts.

EXAMPLE 5

A photographic element as described in Example 2 is sensitometrically exposed and treated with ammonia fumes for a period of 120 seconds at room temperature. A warm black developed image of good density is produced.

EXAMPLES 6-9

Similar results are obtained as described in Example 3 when employing one of the following reaction products in place of the reaction product of ascorbic acid with urea:

EXAMPLE 6 A reaction product of 2,5-dihydroxybenzoic acid with urea

EXAMPLE 7 The reaction product of 1-amino-2-hydroxynaphthalene-6-sulfonic acid with urea

EXAMPLE 8 The reaction product of ascorbic acid with formamide

EXAMPLE 9 The reaction product of 1-amino-2-hydroxynaphthalene-6-sulfonic acid with formamide.

EXAMPLE 10

This illustrates preparation of an ascorbic-acid-guanidine reaction product useful in practice of the invention.

8.8 grams of L-ascorbic acid is dissolved in 100 ml. of ethanol. 5.7 ml. of an ethanol solution of guanidine containing 25 percent by weight guanidine is mixed into the ascorbic acid solution. The resulting mixture is stirred for 30 minutes and then permitted to stand for 30 minutes. The product is a white precipitate which is filtered and washed with ethanol. The product is dried.

EXAMPLE 11

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This illustrates preparation and processing a photographic element of the invention.

A photographic composition is prepared by mixing the following components:

5	Gelatin (aqueous solution containing 7½% by weight gelatin)	40.0 ml.
10	Ascorbic acid-guanidine reaction product (as prepared in Example 10)	2.35 g.
15	Silver chloride emulsion (containing 124 grams of gelatin and 1 mole of silver in each 2.5 kilograms of emulsion)	2.5 ml.
20	Saponin (aqueous solution containing 2% by weight saponin (coating aid))	2.0 ml.

This composition is coated 0.004 inches thick on a paper support and dried.

20 The resulting photographic paper is sensitometrically exposed and the latent image developed by placing the paper on a heated plate for 5 seconds at a temperature of 200° C.

A brown image is produced. The difference between the maximum and minimum density areas is 1.0.

25 The described developing agent precursors employed in the practice of the invention can be employed in combination with suitable fixing and/or stabilizing agents, such as isothiourrea derivatives as described in U.S. Pat. No. 3,220,839 of Herz and Kalenda issued Nov. 30, 1965.

30 The described developing agent precursors can also be employed with developing components which are the reaction product of an alkaline developing agent with a fugitive acid compound, such as the reaction product of cyanoacetic acid with N-methyl-para-aminophenol; oxalic acid with N-methyl-paraaminophenol; and/or malonic acid with N-methyl-paraaminophenol.

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

40 We claim:

1. An element comprising a support having thereon a silver halide emulsion and in said emulsion a preformed thermolabile photographic developing agent precursor which is a reaction product of an ascorbic acid or hydroxytetroneic acid developing agent or a polyhydroxybenzene developing agent containing a carboxyl or sulfonic acid group with an amide or guanidine.

2. An element as in claim 1 wherein said amide is urea.

3. An element comprising a support having thereon a photographic silver halide emulsion and in said emulsion a preformed thermolabile developing agent precursor which is a reaction product of ascorbic acid with an amide or guanidine.

4. A photographic composition comprising a photographic silver salt and a preformed thermolabile photographic developing agent precursor which is a reaction product of ascorbic acid with an amide or guanidine.

5. A photographic composition as in claim 4 comprising a photographic silver halide emulsion.

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