United States Patent Office 3,600,176
Patented Aug. 17, 1971

3,600,176

PHOTOGRAPHIC ELEMENTS, COMPOSITIONS AND PROCESSES

Grant M. Haist and David A. Pupo, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Filed Nov. 29, 1968, Ser. No. 780,231
Int. Cl. G03c 5/30
U.S. Cl. 96—66 16 Claims

ABSTRACT OF THE DISCLOSURE

A developing agent precursor which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent, such as ascorbic acid, or a hydroxytetronic acid silver halide developing agent, such as 5-phenyl-3-hydroxytetronic acid, with (b) a basic aminophenol silver halide developing agent is employed in photographic elements, compositions and processes, especially dry processing with heat. Such a developing agent precursor has the property of being heat activated in the absence of alkali.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to developing agent precursors and to photographic systems containing such precursors. In one of its aspects, the invention relates to elements containing these developing agent precursors. In another of its aspects it relates to photographic compositions, especially photographic silver halide emulsions, containing the described developing agent precursors. A further aspect comprises a method of developing a latent image in a photographic element employing dry processing with heat. It also relates to photographic developer precursor compositions, especially aqueous solutions which are activated by heat.

Description of the prior art

In the usual process of photographic development in 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 and the like.

Incorporation of silver halide developing agents in layers of photographic elements is also known. These are developed after 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), pp. 278–311.

The use of light sensitive silver halide emulsion layers which contain a developing agent and in which the latent image can 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 incorporated in a photographic element, and a free base developing agent is produced upon heating to decarboxylation temperature as described in U.S. Pat. 3,220,846 of Tinker and Sagura issued Nov. 30, 1965. The use of developing agents such as ascorbic acid and 1-phenyl-3-pyrazolidone in photographic elements for dry processing which are subjected to heat are also disclosed in U.S. Pat. 3,041,170 of Haist and King issued June 26, 1962. Mixtures of hydroquinone with 1-phenyl-3-pyrazolidone or ascorbic acid with 1-phenyl-3-pyrazolidone in photographic elements for dry processing are also disclosed in British Pat. 930,572 published July 3, 1963. Combinations of ascorbic acid developing agents with 3-pyrazolidone developing agents are further disclosed in British Pat. 778,792; French Pat. 1,500,987 and French Pat. 1,500,988.

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 cannot be suitably stored and lose desired sensitometric properties.

On the other hand, attempts to employ free base developing agents, such as N-methyl-p-aminophenol in its free base form, provides an unsuitable photographic coating. These are ordinarily neutralized with a strong acid, such as hydrochloric or sulfuric acid to provide a suitable form for development.

In coatings designed for dry processing with heat, the quantity of available alkali for activating developing agents present is very low even in the presence of so-called alkali generating compounds. Furthermore, the use of such alkali generating compounds is in some cases undesirable due to the problems of instability in the coatings. Thus, neutralized developer salts, such as neutralized N-methyl-p-aminophenol is usually not suitable in coatings alone as a developing agent except when activated by significant concentrations of alkali.

There has accordingly been a continuing need for components, especially developing agent precursors, that (a) can be employed in photographic systems, especially photographic coatings, and be easily activated by heat without the need of a separate alkali generating compound or separate source of alkali, (b) provide an acidic developing agent, such as a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic silver halide developing agent, (c) and 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 activated by heat without the need of a separate alkali generating compound or alkali.

It is also an object of the invention to provide photographic emulsions containing such developing agent precursors which can be suitably stored and do not lose desired sensitometric properties under conditions of storage and use.

SUMMARY OF THE INVENTION

In accordance with the invention, a stable, developing agent precursor which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent, such as ascorbic acid, or a hydroxytetronic acid silver halide developing agent, such as 5-phenyl-3-hydroxytetronic acid, with (b) a basic aminophenol silver halide developing agent employed in photographic elements, compositions and processes, especially dry processes, has the property of being heat activated in the absence of alkali and/or

alkali generating materials. The developing agent precursors of the invention are suitable for dry processing, thus eliminating the need for any developer solutions or alkali normally employed to activate developing agents.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

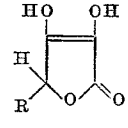
The exact nature of the developing agent precursors of the invention is not fully understood. It is believed a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with (b) a basic aminophenol silver halide developing agent is in some complex or associated form.

The described developing agent precursors are typically prepared by reacting a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with an aminophenol silver halide developing agent in basic or alkaline form. These components are usually reacted in stoichiometric concentrations but concentrations outside these can be employed. The reaction is normally carried out under ambient conditions in a suitable solvent, such as water, and the desired product is separated employing common separation techniques. Preparation of a developing agent precursor which is the reaction product of ascorbic acid with N-methyl-p-aminophenol is exemplary of a suitable process for preparing developing agent precursors of the invention. According to this process an aqueous solution of sodium carbonate monohydrate and sodium sulfite is first prepared. Ethyl acetate and a stoichiometric concentration of N-methyl-p-aminophenol sulfate or hydrochloride is mixed into the aqueous sodium carbonate and sulfite solution and the resulting two phase composition is vigorously mixed together. The mixture is then allowed to separate into an upper and lower phase. The upper phase, which is an ethyl acetate solution of basic N-methyl-p-aminophenol, is separated. This upper phase is added slowly to an aqueous methanol-ascorbic acid solution containing a stoichiometric concentration of ascorbic acid. The resulting solution is allowed to stand at ambient temperature and pressure until reaction completion producing a faint yellow colored solution. The desired reaction product is then separated by removing the solvent from the reaction mixture by suitable means, such as a rotary vacuum evaporator.

The described developing agent precursors can be prepared employing various 3,4-dihydroxy furan silver halide developing agents or hydroxytetronic acid silver halide developing agents which include:

3,4-dihydroxy furan developing agents or hydroxy tetronic acid developing agents of the formula:

(I)



wherein R is aryl containing up to 20 carbon atoms, e.g., 6 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 or hydrogen when n is 2 to 4 and hydroxyl when n is 1.

Suitable 3,4-dihydroxy furan developing agents or hydroxytetronic acid developing agents include:

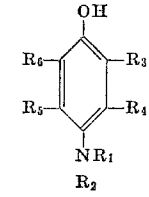
(i) ascorbic acid, e.g., isoascorbic acid, 1-ascorbic acid, and d-ascorbic acid, and ascorbic acid developing agents set out in U.S. Pat. 2,688,549 of James et al. issued Sept. 7, 1964,

(ii) 5-phenyl-3-hydroxytetronic acid; and

(iii) 5-naphthyl-3-hydroxytetronic acid.

A wide range of basic aminophenol developing agents can be employed for preparing the described developing agents precursors. Basic aminophenol developing agents include such developing agents which are not in an acid salt form, e.g., are not in their hydrochloride or sulfate salt form. Suitable basic aminophenol developing agents employed in preparing the described developing agent precursors include, for example, aminophenol developing agents of the formula:

(II)



wherein R_1 and R_2 are the same or different, and each is hydrogen or alkyl, e.g., alkyl containing 1 to 5 carbon atoms, such as methyl, ethyl, propyl, butyl and pentyl; R_3 and R_6 are the same or different, and each is hydrogen, alkoxy, e.g., alkoxy containing 1 to 5 carbon atoms, such as methoxy, ethoxy, propoxy, butoxy and pentoxy, alkyl, as described, or amino, i.e., $—NH_2$, $—NHR_7$ or



wherein R_7 and R_8 are alkyl containing 1 to 5 carbon atoms, such as methyl, ethyl, propyl, butyl and pentyl; R_4 and R_5 are the same or different and each is hydrogen or alkyl, as described. Alkyl or aryl, as described, can include various substituent groups which do not adversely affect the properties of the developing agent precursor, such as hydroxy or alkoxy, as described.

Examples of suitable basic aminophenol developing agents include:

p-aminophenol,
o-aminophenol,
2-methyl-p-aminophenol,
N-methyl-p-aminophenol,
N-methyl-o-aminophenol,
N,N-dimethyl-p-aminophenol,
N-ethyl-N-beta-hydroxyethyl-2-methyl-p-aminophenol,
N,N,2-trimethyl-p-aminophenol,
N,N-diethyl-2-methoxy-p-aminophenol,
N-ethyl-N-beta-hydroxyethyl-p-aminophenol,
2,4-diaminophenol, and
6-methyl-2,4-diaminophenol.

Examples of other aminophenol developing agents are described, for instance, in Mees and James, "The Theory of the Photographic Process," 3rd edition (1966) pages 290–291.

Suitable developing agent precursors which can be employed in the practice of the invention include a reaction product of:

ascorbic acid with N-methyl-p-aminophenol,
ascorbic acid with N,N-diethyl-p-aminophenol,
ascorbic acid with 2-methyl-p-aminophenol,
ascorbic acid with N-ethyl-N-beta-hydroxyethyl-2-methyl-p-aminophenol,
ascorbic acid with p-aminophenol, and/or
5-phenyl-3-hydroxytetronic acid with N-methyl-p-aminophenol.

The described 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 developing agent precursor which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent, such as ascorbic acid, or a hydroxytetronic acid silver halide developing agent, such as 5-phenyl-3-hydroxy-tetronic acid with (b) a basic amino-

phenol silver halide developing agent, the reaction product having the property of being heat activated in the absence of alkali.

The described developing agent precursors can be employed in various layers of an element, e.g., in a photographic layer such as 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 heating of the developing agent precursor.

According to this embodiment an element, especially a photographic element, can comprise a support and a developing agent precursor which is a reaction product of ascorbic acid with a basic N-methyl-p-aminophenol silver halide developing agent, the reaction product having the property of being heat activated in the absence of alkali.

If desired, the described 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 developing agent precursor, which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent, as described, with (b) a basic aminophenol silver halide developing agent, the reaction product having the property of being heat activated in the absence of alkali.

The described developing agent precursors can be used in a wide range of photographic emulsion. These precursors are useful in developing and/or incorporation in X-ray or other non-spectrally 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. 2,526,632 of Brooker et al. issued Oct. 24, 1950 and U.S. 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 bromoiodide, silver chloroiodide, 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. 2,322,027 of Jelley et al. issued June 15, 1943, and U.S. Pat. 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 supports. 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 and/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 poly-saccharides, cellulose derivatives, proteins, water-soluble polyacrylamides, polyvinyl pyrrolidone, 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, sulfoacrylates and the like. 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 butylhydroquinone, 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)-amino; 3 - pyrazolidone developing agents, such as 1-phenyl - 3 - pyrazolidone, including those described in British Pat. 930,572; and acyl derivatives of aminophenols, such as described in British Pat. 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 can be activated if desired with organic or inorganic alkali or alkali generating materials, e.g., materials which release alkali upon heating. For example, the developing agent precursors can be activated with alkali metal hydroxides, such as sodium hydroxide, potassium hydroxide or lithium hydroxide or alkali metal carbonates, such as sodium carbonate or potassium carbonate or bicarbonates or with organic alkali, such as amines, guanidine or alkanol amines, such as ethylamine, ethanolamine or iminodiethanolamine. Alkali generating materials, which can be employed in combination with the developing agent precursors, include those described in U.S. Pat. 3,041,170 of Haist and King issued June 16, 1962; British Pat. 930,572 published July 3, 1963; and Belgian Pat. 709,900. These include, for instance, guanidinium salts and thiuronium alkane sulfonates which have the property of releasing alkali upon heating to above about 90° C., e.g., about 90° C. to about 250° C. Examples of such materials include 3-S-thiuronium propane sulfonate and beta-isothioureidopropionic acid. Such compounds also have the advantage of stabilizing the resulting developed image.

The described developing agent precursors are typically employed in one or more layers of a photographic element, which, after exposure, is heated to cause desired development. Accordingly, a photographic element of the invention is highly suitable for use in dry processing systems. 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, carbonate or organic alkali as described.

The developing agent precursors employed in the practice of the invention are stable and while present in one or more layers of a photographic element subjected to ambient temperatures do not provide undesired sensitometric properties. However, at elevated temperatures, e.g., about 90° C. or higher, typically between about 90° C.

and about 250° C., the developing agent precursor is activated to provide desired developing action.

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 developing agent precursor which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with (b) a basic aminophenol silver halide developing agent, the reaction product having the property of being heat activated in the absence of alkali, comprising heating the photographic element to a temperature at which the basic aminophenol silver halide developing agent is separated from the reaction product. Heating is normally carried out at temperatures above about 90° C., preferably above about 150° C., e.g., about 150° C. to about 250° C., at which temperature the developing agent precursor is activated.

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 upon 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, 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 antifoggant 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 mercaptoazoles. An inorganic antifoggant, such as potassium bromide, potassium iodide and/or sodium bromide can be employed if desired. A suitable concentration of antifoggant can vary depending upon the factors described, but usually a concentration of less than about 2% by weight of antifoggant, e.g., 0.01 to 2% by weight is suitable.

The described silver halide emulsions can also contain antifoggants, such as azaindenes, 4-thiazoline-2-thiones and their related 2,2'-dithio-bisthiazoles, 4-hydroxythiazolidine-2-thiones and their related dithiocarbamates, monothio- or dithio-urazoles, e.g., the alkyl, aryl, acylated, or aroylated derivatives, 2-thiobenzthiazolyl-substituted napthohydroquinones, 4 - thiopyrimidines, 4,4'-dithio-bispyrimidines, enamineacyl isothiocyanates, substituted pyrimidines, e.g., 2-thio and 4-thio derivatives (preferably said pyrimidines or isocyanates being in combination with a tetraazaindene), and organo lead compounds, e.g., trialkyl-N-containing-heterocyclic lead or triarylalkylthio (or arylthio) lead derivatives. Nitro-substituted heterocyclic compounds, preferably the cyanine and merocyanine dye derivatives, e.g., 1,3-diethyl-6-nitrothia-2'-cyanine, are also useful as antifoggants in photographic silver halide photographic emulsions particularly processed in a hardening developer.

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 or developing agent precursors can be employed in the practice of the invention, e.g., in the described photographic elements and compositions. For example, a heat activatable developer can be prepared by reactivating an aminophenol developing agent such as N-methyl-p-aminophenol with a sulfite or bisulfite compound, such as sodium sulfite or sodium bisulfite to form a reaction product which can be employed as a component of the system described. Such reaction products are useful in photographic elements and/or compositions for dry processing.

Other developing agents or developing agent precursors which can be employed in photographic elements, compositions or processes as described include reaction products of ascorbic acid silver halide developing agents with 3-pyrazolidone developing agents, such as 3-pyrazolidone developing agents described in British Pat. 930,572, e.g., 1-phenyl-3-pyrazolidone or 1-phenyl-4,4-dimethyl-3-pyrazolidone; or reaction products of a polyhydroxybenzene developing agent, such as hydroquinone, catechol, 4-phenylcatechol or tertiary-butylhydroquinone with a 3-pyrazolidone developing agent as described. These are useful in any suitable location in the described photographic systems and are especially suitable for dry processing.

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

EXAMPLE 1

This example illustrates preparation of developing agent precursors of the invention.

50 grams of sodium carbonate monohydrate and 30 grams of sodium sulfiite are sequentially added to 500 milliliters of distilled water in a flask. The admixture is stirred until the components are dissolved. 500 milliliters of ethyl acetate and 50 grams of N-methyl-p-aminophenol sulfate are sequentially added to the flask. The solution is then vigorously agitated. Two phases are formed. The phases formed are separated using a separatory funnel. The upper phase comprising ethyl acetate and N-methyl-p-aminophenol is retained.

52 grams of ascorbic acid is added to 200 milliliters of ethanol and 20 milliliters of distilled water in a beaker. The mixture is stirred until a solution is formed. Next, the ethyl acetate phase containing N-methyl-p-aminophenol, previously prepared, is slowly added to the ascorbic acid solution. The solution is allowed to stand. The solvent in the mixture is then removed employing a rotary vacuum evaporator. The resulting liquid is yellow-orange in color, and comprises a complex of ascorbic acid with N-methyl-p-aminophenol.

EXAMPLE 2

A photographic composition is prepared by mixing the following components:

Ingredient:	Concentration
Sucrose ---------- g--	1.5
Citric acid ---------- g--	0.2
Distilled water ---------- g--	20.0
Gelatin, 5% by weight aqueous solution ---------- ml--	20.0
Ascorbic acid-N-methyl-p-aminophenol complex (as prepared in Example 1) ---- ml--	1.6
Silver chloride emulsion [1] ---------- ml--	2.0

[1] A fine grain silver chloride emulsion containing one mole of silver per 125 grams of gelatin in each 2.5 kg. of emulsion.

A small concentration of saponin (2% by weight) is added to the resulting composition as a coating aid and the mixture is filtered. The resulting composition is then coated on a paper support at a wet thickness of 0.006 inch. The resulting photographic element is then dried.

EXAMPLE 3

The procedure set out in Example 2 is repeated with the exception that a polyethylene terephthalate film base is employed in place of the paper support.

EXAMPLE 4

A strip of the photographic paper prepared as described in Example 2 is sensitometrically exposed and the side opposite the photographic coating is contacted with a heated block having a surface temperature of 155° C. for a period of 30 seconds.

A dark brown image having good density with a tannish background is produced.

EXAMPLE 5

A strip of the photographic element as described in Example 3 is sensitometrically exposed. The element is then heated by placing the side opposite the photographic coating in contact with a heated block having a surface temperature of 155° C. for a period of 15 seconds.

A dark brown image of good density with a tannish background is produced.

EXAMPLE 6

This is a comparative example.

A photographic element is prepared as described in Example 2 with the exception that 0.8 gram of N-methyl-p-aminophenol sulfate and 0.8 gram of ascorbic acid is used in place of 1.6 milliliters of a complex as prepared in Example 1, i.e., in place of a complex of ascorbic acid with N-methyl-p-aminophenol.

The resulting photographic element is dried and sensitometrically exposed. It is then heated by passing the side opposite the photographic coating over a heated block having a surface temperature of 155° C. for a period of 30 seconds.

An extremely brownish image with an orange background is produced. In comparison to the photographic elements prepared and processed according to the invention, a very poor image is obtained with photographic coatings containing the described individual developing agents.

EXAMPLE 7

This illustrates that the developing agent precursors described can be employed in solutions for so-called wet processing.

49 grams of N-methyl-p-aminophenol sulfate is added to 500 milliliters of distilled water in a beaker. The mixture is heated to a temperature of 60° C. to form a solution. Then 31 grams of ascorbic acid is added to the solution with stirring. Then 12.5 grams of sodium carbonate monohydrate is added with stirring to the resulting solution. The mixture is cooled by the addition of refrigerated water to a temperature of 9° C. and is permitted to stand for a period of one hour. Small white crystals of the desired reaction product, which is a complex of ascorbic acid with N-methyl-p-aminophenol precipitate from the solution and are removed by filtration. The crystals are then dried.

One gram of the described white crystals is mixed into 50 milliliters of distilled water to form a heat activatable developing agent precursor solution.

A strip of exposed fine grain photographic film is sensitometrically exposed with a commercial sensitometer and then placed in the resulting solution for 5 minutes at 24° C. No visible image is formed.

The developer precursor solution is then heated to about its boiling temperature for a period of 90 seconds. A second strip of identical fine grain photographic film is sensitometrically exposed and placed in the solution which is at a temperature of 80° C. A visible image is formed in about 2 minutes consisting of finely divided brownish silver of low density.

The developing solution is then cooled to a temperature of 24° C. and a third strip of photographic film (Kodak Panatomic-X Film) is sensitometrically exposed and placed in the solution for a period of 5 minutes. No visible image is formed.

This illustrates the developing agent precursors employed in the practice of the invention can be employed in developer compositions which are heat activated.

EXAMPLE 8

A photographic element is prepared as described in Example 2 with the addition of 2 g. of 3-S-thiuronium-propane sulfonate to the described composition.

The element is sensitometrically exposed and heated as described in Example 4 to produce a developed light-stable image.

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.

We claim:

1. A photographic silver halide element comprising a support and a developing agent precursor which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with (b) a basic aminophenol silver halide developing agent, said reaction product having the property of being heat activated in the absence of alkali.

2. An element as in claim **1** also comprising a thiuronium alkane sulfonate.

3. An element as in claim **1** comprising a support and a developing agent precursor which is a reaction product of ascorbic acid with a basic N-methyl-p-aminophenol silver halide developing agent, said reaction product having the property of being heat activated in the absence of alkali.

4. A photographic element as in claim **1** comprising a support, sucrose, citric acid, a reaction product of ascorbic acid with an N-methyl-p-aminophenol silver halide developing agent and photographic silver halide emulsion.

5. A photographic composition comprising a photographic silver halide and a developing agent precursor which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with (b) a basic aminophenol silver halide developing agent, said reaction product having the property of being heat activated in the absence of alkali.

6. A photographic composition as in claim **5** wherein said developing agent precursor is a reaction product of ascorbic acid with a basic N-methyl-p-aminophenol silver halide developing agent.

7. A photographic composition as in claim **6** comprising a photographic silver halide emulsion.

8. A photographic composition as in claim **5** comprising sucrose, citric acid, a reaction product of ascorbic acid with an N-methyl-p-aminophenol silver halide developing agent and photographic silver halide emulsion.

9. A method of developing a latent image in a photographic element comprising a support, an exposed photographic silver halide and a developing agent precursor which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with (b) a basic aminophenol silver halide developing agent, said reaction product having the property of being heat activated in the absence of alkali, comprising heating the photographic element to a temperature at which the basic aminophenol silver halide developing agent is separated from the reaction product.

10. A method as in claim **9** wherein the developing agent precursor is a reaction product of ascorbic acid with a basic N-methyl-p-aminophenol silver halide developing agent.

11. A method as in claim **9** comprising heating the element to at least about 90° C.

12. A method as in claim **9** of developing a latent image in a photographic element comprising a support, sucrose,

citric acid, a reaction product of ascorbic acid with an N-methyl-p-aminophenol silver halide developing agent and photographic silver halide emulsion comprising heating said element to 90° C. to 250° C. for about 1 second to about 1 minute.

13. A method of developing a latent image in a photographic element comprising a support, an exposed photographic silver halide and a developing agent precursor which is a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with (b) a basic aminophenol silver halide developing agent, comprising contacting the element with an alkaline development activator.

14. A photographic developer precursor composition comprising a neutral or acidic aqueous solution of a reaction product of a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with a basic aminophenol silver halide developing agent, the composition having the property of being active with the application of heat.

15. A photographic developing agent precursor comprising a reaction product of (a) a 3,4-dihydroxy furan silver halide developing agent or a hydroxytetronic acid silver halide developing agent with (b) a basic aminophenol silver halide developing agent, said developing agent precursor having the property of being activated in the absence of alkali.

16. A photographic developing agent precursor as in claim **15** comprising a reaction product of ascorbic acid with an N-methyl-p-aminophenol silver halide developing agent.

References Cited

UNITED STATES PATENTS

2,327,773	8/1943	Dickey et al.	96—66X
2,688,548	9/1954	Reynolds	96—66
2,688,549	9/1954	James et al.	96—66
3,041,170	6/1962	Haist et al.	96—66
3,178,282	4/1965	Luckey et al.	96—66X
3,220,846	11/1965	Tinker et al.	96—91
3,265,499	8/1966	Willems et al.	96—66X
3,291,609	12/1966	Porter et al.	96—66X
3,415,651	12/1968	Konig et al.	96—66X
3,490,905	1/1970	Blake	96—66X

FOREIGN PATENTS

778,792	7/1957	Great Britain	96—66
858,432	1/1961	Great Britain	96—66
930,572	7/1963	Great Britain	96—66

WILLIAM D. MARTIN, Primary Examiner

M. R. LUSIGNAN, Assistant Examiner

U.S. Cl. X.R.

96—95