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3,041,170

NEW CLASS OF DEVELOPMENT PROMOTER PRECURSORS FOR DRY PROCESSING SELF-DEVELOPING SILVER HALIDE COATINGS

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This invention relates to photography and particularly to self-developing photographic emulsions containing a new class of development promoter precursors and to a method for the "dry" processing of these emulsions.

It has long been known that photographic developing agents, such as hydroquinone, can be incorporated in light-sensitive photographic emulsions so that these emulsions after exposure, can be developed simply by immersing in alkaline solutions. The processes used to develop these emulsions may be referred to as "wet" processes.

It is also known that light-sensitive emulsions containing incorporated developer can be made which are developed by "dry" processing. By "dry" processing we mean that no liquid processing solutions are required in the development of the photographic image. Photographic materials designed for "dry" processing contain incorporated developing agents and a compound which we call a development promoter precursor that activates the developing agent upon the application of heat. Development promoter precursors do not activate the developing agent until heat is applied during development. Application of heat to known development promoter precursors is believed to cause them to release ammonia or an amine which serves to activate the incorporated developing agent which, then develops exposed silver halide. Fierke and Staud, for example, in U.S. Patent 2,410,644, issued November 5, 1946, describe the use of compounds such as betaines, tetramethylammonium iodide, and diaminobutane dihydrochloride. It is known that compounds having the formula R_4NX are useful as development promoter precursors. In this formula R represents alkyl, e.g., methyl, ethyl, hydroxyethyl, higher alkyl or aryl groups, and X is any anion that does not interfere with the photographic image formation. Any of the tetramethyl or tetraethyl ammonium salts, are useful but preferably not with halogen anions.

It is an object of the present invention to provide photographic silver halide emulsions containing a developing agent and a new class of development promoter precursor compounds which make possible "dry" development of a silver image without need for liquid processing solutions merely by heating the exposed emulsion, for example by application of steam, by immersion in a molten paraffin bath, or by exposure to a surface heated to a temperature of about 300° F., etc.

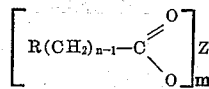
It is an object of the invention to provide a new class of development promoter precursor compounds which when incorporated in self-developing photographic elements will promote a more rapid "dry" development than is possible with known development promoter precursors.

It is a further object to provide a new class of development promoter precursor compounds which can be conveniently incorporated in a self-developing silver halide emulsion layer, in an emulsion layer in intimate contact with a self-developing photographic emulsion layer, in the support upon which the self-developing emulsion is coated or in combinations of these strata.

It is a still further object of the present invention to provide a new class of development promoter precursors which may be used in conjunction with prior art development promoter precursors in self-developing photographic emulsions which are processed by "dry" methods.

A further object of the invention is to provide a method for "dry" processing of light-sensitive photographic elements containing development promoter precursors of our invention. Other objects will be apparent from the following description and claims.

According to our invention, there is incorporated in a light-sensitive photographic element containing a silver halide emulsion, and a developing agent, a salt of an organic acid which is capable of promoting photographic development when subjected to heat. The developing agent may be any of the suitable, known compounds, such as hydroquinone, p-methylaminophenol sulfate 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, etc. The developing agent may be a single compound or a mixture of two or more developing compounds, for example, hydroquinone and 1-phenyl-3-pyrazolidone, p-methylaminophenol sulfate and ascorbic acid, 1-phenyl-3-pyrazolidone and dihydrofuran. Mixtures of 1-phenyl-3-pyrazolidone and ascorbic acid give preferred results. The salt of the organic acid which we use as a development promoter precursor may be a compound which, upon heating, releases an alkaline substance such as sodium hydroxide or sodium carbonate, or may be a compound which in other ways promotes development of the exposed silver halide grains by the incorporated developing agent. The development promoter precursor compounds of our invention have the following general formula:



wherein R represents a hydrogen atom, an aryl group, such as phenyl, a carboxyl group and a salt of a carboxyl group, such as the sodium, potassium, and ammonium salts; n is an integer of from 1 to 6 and Z is an alkali metal, such as sodium, and potassium, a boron atom or an ammonium radical, and m is the integer 1 or 3, representing 1 when Z is a radical having a single valence and 3 when Z represents a boron atom.

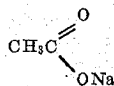
Development promoter precursor compounds of our invention which we have found particularly useful according to our invention are illustrated by the following, however, it is to be understood that our invention is not to be limited in any way by these illustrated compounds.

COMPOUND I



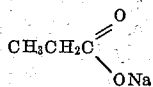
sodium formate

COMPOUND II



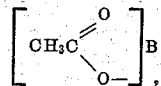
sodium acetate

COMPOUND III



sodium propionate

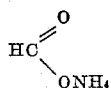
COMPOUND IV



boron triacetate

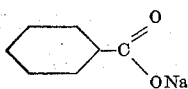
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COMPOUND V



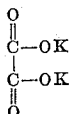
ammonium formate

COMPOUND VI



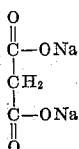
sodium benzoate

COMPOUND VII



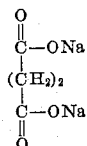
dipotassium oxalate

COMPOUND VIII



disodium malonate

COMPOUND IX



disodium succinate

The compounds of our invention may be prepared by well known procedures. Many of these compounds are available commercially.

The compounds of our invention appear to act differently from the prior art development promoter precursor compounds such as those represented by the formula R_4NX . Our compounds appear to act as development promoters when they are heated during "dry" development and are characterized by being effective in this capacity at temperatures at which the compounds having the formula R_4NX are incapable of causing development to occur. It is known that upon heating, sodium formate releases sodium carbonate and that sodium acetate releases sodium hydroxide. The exact mechanism by which the other compounds of our invention work is not completely understood. However, it is believed that these other compounds do not decompose as do sodium formate and sodium acetate. The compounds of our invention are characterized as being distinct from the compounds having the formula R_4NX in that they do not release amines as do the latter compounds.

Not only are our compounds characterized by being capable of promoting development at temperatures lower than many of the prior art compounds, but they are also notably faster acting than many of the prior art compounds. For example, the "dry" development step of our process requires only from 10 to 30 seconds of heating as compared to 3 or 4 minutes of heating required by self-developing emulsions containing some of the prior art development promoter precursor compounds.

The development promoter precursor compounds of our invention can be incorporated in the light-sensitive photographic emulsion layer, in a separate layer, in the paper base or may be incorporated in combinations of these. For example, our compounds may be incorporated in the emulsion layer containing the light-sensitive silver

4

halide and developing agent coated on a suitable support, or they may be incorporated in a separate layer that is coated either on top of or underneath the emulsion layer containing the light-sensitive silver halide and the incorporated developer, or our compounds may be incorporated in the paper base over which is coated the emulsion containing light-sensitive silver halide and incorporated developing agent. When the development promoter precursor compound is incorporated in more than one strata of a self-developing photographic element, it is possible to use several different compounds if desired or larger quantities of a single compound can be used than would otherwise be possible.

The compounds of our invention are not in themselves alkaline but are more or less neutral. However, it is important that the optimum pH value of a photographic emulsion not be disturbed by the addition of addenda, such as our compounds. Generally the pH of a gelatin dispersion containing the desired development promoter precursor is determined by some suitable means, such as with a Beckman pH meter, for example, and its pH is then adjusted to within 0.1 pH unit of the pH of the emulsion to which it will be added. The adjustment of pH can be accomplished by suitable additions of acetic acid, hydrochloric acid or sodium hydroxide.

Emulsions containing our development promoting precursor compounds can be coated on any suitable support such as paper, glass or film.

The photographic emulsions used in practicing our invention are of the developing-out type.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926, Sheppard et al. U.S. Patent 1,623,499, issued April 5, 1927, and Sheppard et al. U.S. Patent 2,410,689, issued November 5, 1946.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952. Suitable compounds are potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethyl triamine (Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(β -aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950, and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950, and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Mur-

ray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents 2,444,607, issued July 6, 1948 and 2,450,397, issued September 28, 1948; Heimbach and Clark U.S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patents 2,713,541, issued July 19, 1955, and 2,743,181, issued April 24, 1956; Carroll and Beach U. S. Patent 2,716,062, issued August 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," Vol. 47, 1952, pages 2-28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938, or the polymethylene bis-benzothiazolium salts of Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g. decamethylene-bis-benzothiazolium perchlorate); or the zinc and cadmium salts of Jones U.S. Patent 2,839,405, issued June 17, 1958.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. application Serial No. 588,951, filed June 4, 1956, now U.S. Patent 2,960,404, issued November 15, 1960; an ester of an ethylene bis-glycolic acid such as ethylene bis-(methyl glycolate) as described in Milton U.S. application Serial No. 662,564, filed May 31, 1957 now U.S. Patent 2,904,434, issued September 15, 1959; bis-(ethoxy diethylene glycol) succinate as described in Gray U.S. application Serial No. 604,333, filed August 16, 1956, now U.S. Patent 2,940,854, issued June 14, 1960, or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong. U.S. Patent 2,852,386, issued September 16, 1958. The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsions may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo (2,2,2)-7-octene-2,3,5,6-tetra-carboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonoyl chloride as described in Allen and Carroll U.S. Patents 2,725,294, and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di-(methanesulfonyl)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxy methylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2-3 carbon atoms, such as β -methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness U.S. Patent application Serial No. 556,031, filed December 29, 1955; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. Patent application Serial No. 559,891, filed July 25, 1956 now U.S. Patent 2,950,197, issued August 23, 1960; or 2,3-dihydroxy dioxane as described in Jeffreys U.S. Patent 2,870,013, issued January 20, 1959.

The emulsions may contain a coating aid such as

saponin; a lauryl or oleyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. Patent 2,843,487, issued July 15, 1958; a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamate salt as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert. octylphenoxypentaethoxy)-glutamate as described in Knox and Wilson U.S. Patent application Serial No. 600,679, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox and Stenberg U.S. Patent application Serial No. 691,125, filed October 21, 1957 now U.S. Patent 2,992,108, issued July 11, 1961.

The photographic development promoter precursors which we have described may be used in various kinds of photographic emulsions. In addition to being useful in X-ray and other nonoptically sensitized emulsions they may also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They may be added to the emulsion before or after any sensitizing dyes which are used. 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 bromiodide. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794, issued January 4, 1955; or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

They may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,698,236, issued December 28, 1954, and 2,543,181, issued February 27, 1951; and Yachel et al. U.S. patent application Serial No. 586,705, filed May 23, 1956, now U.S. Patent 3,020,155, issued February 6, 1962. They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951, and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Patents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 16, 1957 and 554,935, granted August 12, 1957; Yutzy U.S. Patent

2,756,142, granted July 24, 1956, and Whitmore and Mader U.S. Patent application Serial No. 734,141; filed May 9, 1958.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19-26% as described in U.S. Patent 2,327,808, of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamine having a combined acrylamide content of 30-60% and a specific viscosity of 0.25-1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,382, of Illingsworth, Dann and Gates, issued September 16, 1958.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation. Combinations of these antifoggants, sensitizers, hardeners, etc., may be used.

If desired the image developed by "dry" processing in the photographic elements of our invention may be stabilized by using techniques which are disclosed in Fierke and Staud U.S. Patent 2,410,644, or by the technique disclosed in Stewart, Fallesen and Reeves U.S. Serial No. 805,582, filed April 10, 1959. The preferred techniques involve the incorporation of an alkali, or an aryl iodide or a hexamethylene tetramine allyliodide or other quaternary ammonium salt of such active iodide, as disclosed by Fierke and Staud, or the incorporation of mercaptan compounds as disclosed by Stewart, Fallesen, and Reeves.

The following examples will serve to illustrate more fully the manner in which the development promoter precursors of our invention are used in photographic emulsions and how these emulsions are developed by "dry" processing techniques. In preparing the light-sensitive emulsions for these examples in which development promoter precursors of our invention were incorporated, the pH was adjusted as previously described to the pH of a solution of 20 ml. of 10% photographic gelatin and 20 ml. of H₂O which was found to be about 5.8.

Example I

A dispersion consisting of 20 ml. of photographic gelatin, 20 ml. of water and 3 g. of sodium formate was coated in a 0.005 inch layer on 30-pound paper stock. When this coating was dry, a second layer was coated over it consisting of a filtered dispersion having a pH of 4.4 and the following composition:

Water	-----ml.	20
1-phenyl-3-pyrazolidone	-----g.	0.2
1-ascorbic acid	-----g.	0.4
Sucrose	-----g.	2.0
10% photographic gelatin solution in water	-----ml.	20
High speed bromoiodide emulsion	-----ml.	2.0

After drying, this photographic element was given a

stepped exposure and developed by heating the back of the paper on a roller whose surface temperature was 300° F. After 10 seconds' contact a silver image had developed.

Example II

A dispersion consisting of 20 ml. of photographic gelatin, 20 ml. of water and 3 g. of sodium acetate was coated in a 0.006 inch layer on 30-pound paper stock. After this coating was dried, a second layer was coated over it consisting of a filtered dispersion having the following composition:

Water	-----ml.	20
1-phenyl-3-pyrazolidone	-----g.	0.25
1-ascorbic acid	-----g.	0.5
Sucrose	-----g.	1.5
Photographic gelatin	-----ml.	20
High speed bromoiodide emulsion	-----ml.	2.5

After drying, the photographic element was exposed to an image and then heated to 300° F., by applying heat to the back of the paper support. A reddish black image was formed.

Example III

The photographic element of Example I was given a stepped exposure and developed by heating the front of the paper with steam from a steam iron. A silver image appeared in the print after 10 seconds of steaming.

Example IV

The photographic element of Example I was given a stepped exposure and developed by immersing the element for 10 seconds in paraffin heated to 275° F. A silver image was produced.

Example V

A photographic element was made according to the procedure used in Example I except that sodium acetate was used in place of sodium formate. This element was given a stepped exposure and developed by heating with steam for 10 seconds to produce a silver image.

Example VI

A photographic element was made according to the procedure of Example I using sodium propionate in place of sodium formate. This element was given a stepped exposure and developed by heating with steam for 10 seconds to produce a silver image.

Example VII

A photographic element was made according to the procedure of Example I, using boron acetate in place of sodium formate. This element was given a stepped exposure and developed by heating with steam for 10 seconds to produce a silver image.

Example VIII

A photographic element was made according to the procedure of Example I using ammonium formate in place of sodium formate. This element was given a stepped exposure and developed by heating with steam for 10 seconds to produce a silver image.

Example IX

A photographic element was made according to the procedure of Example I using sodium benzoate in place of sodium formate. This element was given a stepped exposure and developed by heating with steam for 10 seconds to produce a silver image.

Example X

A photographic element was made according to the procedure of Example I using dipotassium oxalate in place of sodium formate. This element was given a stepped exposure and developed by heating with steam for 10 seconds to produce a silver image.

Example XI

A photographic element was made according to the procedure of Example I using disodium malonate in place of sodium formate. This element was given a stepped exposure and developed by heating with steam for 10 seconds to produce a silver image.

Example XII

A photographic element was made according to the procedure used in Example I except that disodium succinate was used in place of sodium formate. This element was given a stepped exposure and developed by heating with steam for 10 seconds to produce a silver image.

Example XIII

Similarly, other samples of the photographic element formed in each of the Examples V through XII were given stepped exposures and developed by heating the back of the paper on a roller whose surface temperature was about 300° F. In each case, a silver image resulted after from 10 to 30 seconds' exposure to heat.

Another set of these photographic elements from each of the Examples V through XII were given stepped exposures and developed by immersing them in molten paraffin having a temperature of about 275° F. Silver images were formed in each instance by an immersion of 10 to 30 seconds.

The image produced was nil when an exposed photographic element described in Example I but containing no development promoter precursor was developed by heating with a hot roller (300° F.), by exposure to steam, or by immersion in molten paraffin at about 275° F.

Creatinine, a compound not conforming to the general formula of our development promoter precursors, incorporated in place of sodium formate in the photographic element of Example I did not give an image when the exposed element was developed by heating with a hot roller (300° F.) by exposure to steam, or by immersion in molten paraffin at about 275° F.

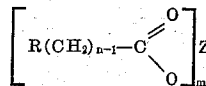
The compounds of our invention are valuable development promoter precursors for use in self-developing photographic elements designed for "dry" development. These compounds are characterized by being easily incorporated in the light-sensitive photographic emulsion layer or in layers adjacent to the light-sensitive photographic emulsion layer. They are further characterized by being very active development promoters when heated to the temperatures used in "dry" development. They are not only effective at temperatures below the temperatures required for prior art development promoters used in self-developing photographic elements, but they result in image development following from 10 to 30 seconds of heating as compared to 3 to 4 minutes or longer of heating required by prior art compounds. Thus they are especially valuable where high-speed development is desired. Our compounds are further characterized by not releasing amines as do many of the prior art blocked alkalies upon heat processing. Amines are odorous, toxic, and the parent compounds are generally less stable at ordinary temperatures than our development promoter precursors.

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 as described hereinabove and as defined in the appended claims.

We claim:

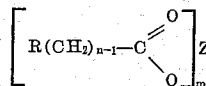
1. A photographic element comprising a support having coated thereon a light-sensitive photographic silver halide emulsion wherein a substantial proportion of silver halide grains are in intimate contact with a photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone and in contact with a development

promoter precursor selected from those having the formula:



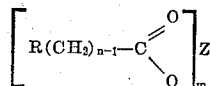
wherein R is a member selected from the class consisting of the carboxy group, the sodium carboxylate group, the potassium carboxylate group and the ammonium carboxylate group; n is a positive integer of from 1 to 6; Z is a member selected from the class consisting of a sodium atom, a potassium atom, a trivalent boron atom, and an ammonium radical; and m is an integer corresponding to the valence of Z.

2. An integral photographic element comprising a support layer, a light-sensitive hydrophilic layer containing photographic silver halide grains in intimate contact with a dispersed photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone and at least one additional hydrophilic layer containing a development promoter precursor selected from those having the formula:



wherein R is a member selected from the class consisting of the carboxy group, the sodium carboxylate group, the potassium carboxylate group and the ammonium carboxylate group; n is a positive integer of from 1 to 6; Z is a member selected from the class consisting of a sodium atom, a potassium atom, a trivalent boron atom, and an ammonium radical; and m is an integer corresponding to the valence of Z, such that said development promoter precursor is in contact with a substantial proportion of said silver halide grains and said developing agent in said light-sensitive hydrophilic layer.

3. A photographic element comprising a paper support having coated thereon a light-sensitive hydrophilic layer containing photographic silver halide grains in intimate contact with a dispersed photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone, said paper support containing a development promoter precursor selected from those having the formula:



wherein R is a member selected from the class consisting of the carboxy group, the sodium carboxylate group, the potassium carboxylate group and the ammonium carboxylate group; n is a positive integer of from 1 to 6; Z is a member selected from the class consisting of a sodium atom, a potassium atom, a trivalent boron atom, and an ammonium radical; and m is an integer corresponding to the valence of Z, such that a substantial proportion of said development promoter precursor is in contact with a substantial proportion of said silver halide grains and said developing agent in said light-sensitive hydrophilic layer.

4. An integral photographic element comprising a support layer, a light-sensitive silver halide emulsion layer having a substantial proportion of silver halide grains in intimate contact with an incorporated photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone and at least one of said layers containing disodium succinate in intimate contact with a substantial proportion of said silver halide grains and said developing agent.

5. An integral photographic element comprising a sup-

11

port layer, a light-sensitive silver halide emulsion layer having a substantial proportion of silver halide grains in intimate contact with an incorporated photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone and at least one of said layers containing disodium malonate in intimate contact with a substantial proportion of said silver halide grains and said developing agent.

6. An integral photographic element comprising a support layer, a light-sensitive silver halide emulsion layer having a substantial proportion of silver halide grains in intimate contact with an incorporated photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone and at least one of said layers containing dipotassium oxalate in intimate contact with a substantial proportion of said silver halide grains and said developing agent.

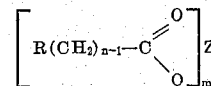
7. An integral photographic element comprising a support layer, a light-sensitive silver halide emulsion layer having a substantial proportion of silver halide grains in intimate contact with an incorporated photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone and at least one of said layers containing dipotassium succinate in intimate contact with a substantial proportion of said silver halide grains and said developing agent.

8. An integral photographic element comprising a support layer, a light-sensitive silver halide emulsion layer having a substantial proportion of silver halide grains in intimate contact with an incorporated photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone and at least one of said layers containing dipotassium malonate in intimate contact with a substantial proportion of said silver halide grains and said developing agent.

9. The method of developing an exposed photographic element comprising a support having coated thereon a hydrophilic layer containing light-sensitive photographic silver halide grains in intimate contact with an incorporated photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and

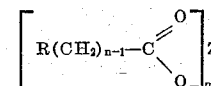
12

a 1-phenyl-3-pyrazolidone and in intimate contact with a development promoter precursor selected from those having the formula:



wherein R is a member selected from the class consisting of the carboxy group, the sodium carboxylate group, the potassium carboxylate group and the ammonium carboxylate group; n is a positive integer of from 1 to 6; Z is a member selected from the class consisting of a sodium atom, a potassium atom, a trivalent boron atom, and an ammonium radical; and m is an integer corresponding to the valence of Z, said method comprising the step of subjecting said exposed element to the action of heat.

10. A method of developing an exposed integral photographic element comprising a support layer, a light-sensitive hydrophilic layer containing photographic silver halide grains in intimate contact with a photographic developing agent selected from the class consisting of hydroquinone, p-methylaminophenol sulfate and a 1-phenyl-3-pyrazolidone and in intimate contact with a substantial proportion of said silver halide grains and said developing agent, as least one hydrophilic layer containing a development promoter precursor selected from those having the formula:



wherein R is a member selected from the class consisting of the carboxy group, the sodium carboxylate group, the potassium carboxylate group and the ammonium carboxylate group; n is a positive integer of from 1 to 6; Z is a member selected from the class consisting of a sodium atom, a potassium atom, a trivalent boron atom, and an ammonium radical; and m is an integer corresponding to the valence of Z, said method comprising the step of subjecting said exposed element to the action of heat.

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