

1

2

3,291,609

**DEVELOPER INCORPORATED PHOTOGRAPHIC MATERIALS**

Ralph Frederick Porter, Pittsford, and Thomas Edward Gompf, Penfield, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed June 5, 1964, Ser. No. 373,050

11 Claims. (Cl. 96-76)

This application is a continuation-in-part of our pending application Serial No. 183,354, filed March 29, 1962, now abandoned.

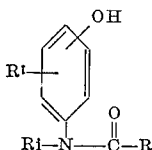
The present invention relates to photographic materials, and to a method of photographic development. More particularly, the present invention relates to developer-incorporated photographic materials and to a method of processing and using the same.

In the usual process of photographic development, the exposed photographic element comprising a support having at least one gelatin silver halide emulsion layer thereon, is immersed in a developing bath containing a silver halide photographic developing agent. The developing bath is normally maintained as a separate processing bath and with continuous use, the bath usually becomes less efficient so that special techniques and replenishments are normally required to maintain optimum processing efficiency. The developing baths of the prior art normally contain a developing agent, a preservative, such as sodium sulfite, and alkali to activate the developing agent, and may also contain other materials, such as sodium bromide (restrainer), antifoggants, etc. The present invention relates to a method of eliminating the usual type of developing bath, and quite unexpectedly obtains optimum results by incorporating certain photographic developing agent-precursors in emulsion layers, or in adjacent layers. The active developing agent is released by alkaline treatment of the layers after exposure.

It is, therefore, an object of the present invention to provide certain developing agent-precursor substances for incorporation in silver halide photographic emulsion layers, or layers adjacent thereto. Another object is to provide silver halide photographic materials which have said precursor substances incorporated in said emulsion layers, or layers adjacent thereto. A further object is to provide processing solutions for the "development" of said emulsion layers. Still another object is to provide a method of processing the emulsion layers of the invention.

The above objects are accomplished by incorporating certain amide compounds in silver halide emulsion layers, or in layers contiguous thereto and, after photographic exposure, treating such layers with an alkaline solution, such as aqueous sodium carbonate, to release active developing agent. The amide compounds of our invention comprise an N-acyl derivative of an aminophenol, preferably a p-aminophenol. The benzene ring of the aminophenol compounds can contain any non-desensitizing conventional substituents (R<sub>2</sub>), such as alkyl (e.g., methyl, ethyl, t-butyl, n-hexyl, n-octyl, etc.), halogen (e.g., chlorine, bromine, etc.), alkoxyl (e.g., methoxyl, ethoxyl, etc.), acylamido (e.g., acetamido, chloroacetamido, trifluoroacetamido, bromoacetamido, etc.), acyloxy (e.g., acetoxy, chloroacetoxy, trifluoroacetoxy), etc. Typical amide compounds of our invention include for example:

(I)



wherein R represents an alkyl group (for example, an alkyl group containing from about 1 to 3 carbon atoms, such as methyl, ethyl, propyl, etc.), or a halogenoalkyl group (for example, a halogenoalkyl group containing from about 1 to 3 carbon atoms, such as chloromethyl, dichloromethyl, trichloromethyl,  $\beta$ -chloroethyl,  $\beta$ -dichloroethyl,  $\beta$ -trichloroethyl, bromomethyl, fluoromethyl, difluoromethyl, trifluoromethyl, etc.), R<sub>1</sub> represents a hydrogen atom or a lower alkyl group, such as methyl, ethyl, propyl, etc. (especially an alkyl group containing from about 1 to 3 carbon atoms), and R<sub>2</sub> represents one or more substituents, such as those enumerated above.

The developer precursor compounds of our invention can be incorporated in an ordinary photographic silver halide emulsion, or colloidal dispersion of a water-permeable hydrophilic colloid suitable for preparing an undercoat or an overcoat for such silver halide emulsion, by mixing a solution or dispersion of the precursor compound with the silver halide emulsion, or dispersion of hydrophilic colloid, prior to coating. For example, a developer precursor can be made up as an oil dispersion by stirring a solution of 10 grams of the developing agent precursor into 40 grams of warm tricresylphosphate, and then mixing this solution with 100 grams of a 10 percent aqueous gelatin solution containing 10 cc. of a 5 percent aqueous solution of an alkylnaphthylene sodium sulfonate wetting agent. The resulting dispersion can then be homogenized by passing for 5 times through a colloid mill to produce a homogeneous colloid dispersion. Solvents other than tricresylphosphate can be employed, including any of the crystalloidal compounds described in Jelley and Vittum U.S. Patent 2,322,027, issued June 15, 1943. The resulting colloidal dispersion can then be added to an ordinary silver halide emulsion, or a dispersion of a water-permeable hydrophilic colloid, adapted for preparation of an undercoat or overcoat for such silver halide emulsion.

Instead of adding the oil dispersion directly to the liquid silver halide emulsion or colloidal dispersion, it can be dried for storage purposes and then be reconstituted for use by merely mixing with water.

The developing agent precursors of our invention can be adapted for addition to a liquid silver halide emulsion or colloidal dispersion by other means as well. Suitable methods will depend largely upon the solubility characteristics, particularly in water or polar solvents, of the particular precursors in question. For example, a 1:1 aqueous methanol solution of p-hydroxyacetanilide can be prepared easily, while less water-soluble material can be dissolved or dispersed more easily in a phenolic solvent, or as an oil dispersion as described above.

After addition of the dispersion or solution of the developing agent-precursor substance to the liquid emulsion or colloidal dispersion, the mixture is stirred to assure uniform results, or passed through a blending device, such as a colloid mill or Waring Blendor. A uniform coating can then be made on a suitable support and the coating dried. Suitable supports comprise any of the well known supporting materials, such as cellulose ester film base (e.g., cellulose acetate, cellulose nitrate, cellulose acetate butyrate, cellulose acetate propionate, etc.), polyethylene, polypropylene, polystyrene, polyethylene terephthalate and other polyesters, paper, polycarbonates, etc.

The photographic elements of our invention comprising a photographic development precursor either in the photographic silver halide emulsion layer, or layer contiguous thereto, or both, can then be exposed to an original or negative and developed by merely treating the exposed emulsion layer with an alkaline activator bath. Typical

activator baths comprise, for example, an aqueous solution of an alkaline material, such as sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, mixtures of sodium hydroxide and sodium sulfite, etc. Suitable baths can comprise, for example an aqueous solution containing about 1 percent sodium hydroxide and 5 percent sodium sulfite. A bath of the latter type is quite suitable for developing an exposed emulsion layer in about 30 seconds when the activator bath is at about 68° F. Modifications can easily be made in the activator baths without departing from the spirit and scope of the invention. For example, an aqueous solution comprising about 4 percent of sodium carbonate and 5 percent of sodium sulfite produces development in about 30 seconds at 68° F. Another aqueous activator solution comprising 2 percent sodium hydroxide and 5 percent sodium sulfite produces useful photographic images in a few seconds when heated at 130° F. Particularly useful activator solutions have a pH of at least about 9.0 and preferably of at least about 10.5.

The activator solutions of the present invention can be applied to an exposed photographic element in any number of known ways, such as by dipping, spraying, or other suitable surface applications. If desired, a thickener can be added to the activator solution to increase the viscosity of the composition and make it more adaptable for continuous processing. Viscous compositions can then be removed by squeegeeing or water spraying. The photographic element can then be stabilized by conventional fixation or stabilization, such as by sodium thiosulfate.

The concentration of the amide compounds used in our invention will vary, depending upon the particular chemical compound involved and the location of the compound within the photographic element. That is, if the amide compound is incorporated within the silver halide emulsion undergoing development, it may be desirable to use a somewhat different concentration than would be used if the amide compound were incorporated in a layer contiguous to the photographic silver halide emulsion. A useful concentration of amide compound for incorporation in the emulsion is from about 0.1 to 4.0 moles per mole of silver halide. A particularly useful range is from about 0.25 to 2.0 moles per mole of silver halide, with especially useful results being obtained within the range of about 0.4 to 1.0 mole per mole of silver halide. For incorporation in layer contiguous to the silver halide emulsion layer, somewhat larger concentrations of amide compound can be tolerated without adverse effects. A particularly useful effect of our invention is that even when incorporated within the silver halide emulsion, the amide compounds of Formula I have little or no desensitizing effects. In many cases, this is not true where developing agents, per se, are incorporated within the silver halide emulsion layers.

Photographic silver halide emulsions useful in our invention comprise any of the ordinarily employed silver halide developing out emulsions, such as, silver-chloride, -chlorobromide, chloriodide, -chlorobromiodide, -bromide and -bromiodide developing-out emulsions. Any of the conventionally employed water-permeable hydrophilic colloids can be employed in the silver halide emulsions, or in layer contiguous thereto. Typical water-permeable hydrophilic colloids include gelatin, albumin, polyvinyl alcohol, agar agar, sodium alginate, hydrolyzed cellulose esters, hydrophilic polyvinyl copolymers, etc.

Photographic silver halide emulsion useful in our invention can also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamate, thiourea, allyl isothiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.). (See U.S. Patents 2,540,085, 2,597,856 and 2,597,915, etc.)

Photographic silver halide emulsions useful in our invention can also be sensitized by other means, such as by alkylene oxide polymers, many of which are well known

to those skilled in the photographic art. Typical polyalkylene oxide polymers include those of U.S. Patents 2,423,549 and 2,441,389.

The emulsions of the invention can also contain speed-increasing compounds of the quaternary ammonium type as described in U.S. Patents 2,271,623, issued February 3, 1942; 2,288,226, issued June 30, 1942; 2,334,864, issued November 23, 1943; or the thiopolymers as described in Graham et al. U.S. Patent No. 3,046,129, issued July 24, 1962, and Dann et al. U.S. Patent 3,046,134, issued July 24, 1962.

The emulsions may also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850), polyamines such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698), polyamines such as spermine (Lowe and Allen U.S. Patent 2,521,925), or bis-( $\beta$ -aminoethyl) sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926).

The emulsions may also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. application Serial No. 319,611; Carroll and Murray U.S. application Serial No. 319,612; and Leubner and Murray U.S. application Serial No. 319,613, all filed November 8, 1952, now U.S. Patents 2,728,663, 2,728,664 and 2,728,665, respectively, granted December 27, 1955.

The addenda 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. 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 9, 1955; or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243.

It has been found that the development rate of the compounds represented by Formula I above sometimes can be improved by adding an auxiliary developing agent either to the silver halide emulsion layer, or a hydrophilic layer contiguous thereto. Typical auxiliary developing agents include those described in Belgian Patent 621,608, issued September 14, 1962, of P. H. Stewart, G. E. Falsen and J. W. Reeves, Jr. Typical auxiliary developing agents described in this patent include 3-pyrazolidone compounds containing an alkyl (e.g., methyl, ethyl, etc.) or aryl substituent (e.g., phenyl, p-tolyl, etc.). In addition, such pyrazolidone developing agents can contain an acyl or acyloxy substituent which can be hydrolyzed from the 3-pyrazolidone compound by treatment with the above activator solutions to produce the desired auxiliary developing compound. Typical auxiliary developing agents include, for example,

- 1-phenyl-3-pyrazolidone,
- 1-p-tolyl-3-pyrazolidone,
- 1-phenyl-3-methyl-3-pyrazolidone,
- 1-acetamidophenyl-3-pyrazolidone,
- 3-acetoxy-1-phenyl-3-pyrazolidone (Enol ester),
- 2-(pyridinium acetyl)-1-phenyl-3-pyrazolidone chloride,
- 1-phenyl-4,4-dimethyl-3-pyrazolidone,
- 1-phenyl-4-methyl-3-pyrazolidone,
- 1-phenyl-2-benzoyl-3-pyrazolidone,
- 1-phenyl-2-lauroyl-3-pyrazolidone,
- 1-phenyl-2-chloroacetyl-3-pyrazolidone, etc.

The concentration of auxiliary developing agents can be varied and, of course, no auxiliary developing agent need be employed unless so desired. Useful concentrations of auxiliary developing agents vary from about 0.01 mole to 2.0 moles per mole of amide compound. De-

5

pending upon the particular auxiliary developing agent employed, larger or smaller quantities can be used.

It has also been found that the development precursors of our invention can be used quite effectively with a development precursor of the hydroquinone type, such as those described in our copending applications Serial Nos. 183,354, filed March 29, 1962, now abandoned, and 366,127, filed May 8, 1964, now U.S. Patent No. 3,246,988. The hydroquinone type of development precursor includes those wherein one or both of the phenolic hydroxyl radicals has been esterified with an organic acid, anhydride or halide, as described in such applications. The esterification can be accomplished by means which have already been described in the prior art, where a reaction mixture containing both hydroquinone compound and organic acid, anhydride or halide is heated, preferably in the presence of a basic condensation agent. The resulting mono- or di-esters can then be used together with the amide development precursors of this application. In general, the quantity of development precursor of the hydroquinone type can be from about 10 to about 200 mole percent of the quantity of amide precursor. The hydroquinone type of development precursor can be incorporated in the photographic elements of our invention in the manner described below. Organic acids which can be used as such, or in the form of their anhydrides or halides, to esterify the hydroquinone compound include acids, such as acetic, propionic, butyric, etc., which may have one or more halogen substituents on the carbon atoms of such acids. Typical halogen substituents include chlorine, bromine and fluorine, for example.

The amide derivatives of Formula I above can easily be prepared by reacting an organic acid, an anhydride or halide with the corresponding aminophenol compound (nuclear substituted or unsubstituted).

The following examples will serve to illustrate the preparation of typical amide compounds or intermediates.

#### Example 1

p-(N-methyl-N-trifluoroacetyl)aminophenol for incorporating in a silver halide emulsion layer according to the invention was prepared by adding 14 g. of p-methylaminophenol to 100 ml. of trifluoroacetic anhydride resulting in an exothermic reaction and forming a dark solution which was maintained at reflux for about two and a half days. The solvent was evaporated from the solution yielding a heavy oil that was triturated with 100 ml. of cold water. The resultant oil was air dried to produce a crystalline solid having a melting point of 109–111° C. and was crystallized from chloroform-ligroin to yield 17.21 g. of pinkish-white prisms having a melting point of 103–104° C.

Analytical calculation for  $C_9H_9O_2NF_3$ : C, 49.4; H, 3.68; N, 6.40. Found: C, 49.2; H, 3.8; N, 6.6, 6.7.

#### Example 2

p-(N-trifluoroacetyl)aminophenol suitable for use as an incorporated developer precursor according to the present invention was prepared by adding 250 g. of trifluoroacetic anhydride dropwise into a vessel containing 54.6 g. p-aminophenol after which the mixture was stirred and maintained at 5° C. and refluxed continuously overnight. After cooling, the solution was poured into 750 ml. of ice water to give a brown oil. The aqueous phase was decanted, the oil washed rapidly with warm water and subsequently evaporated to dryness with 500 ml. of benzene. The oil was crystallized from acetone-benzene and recrystallized from chloroform several times to give 12.72 g. of white flakes having a melting point of 173.5–174° C.

Analytical calculation for  $C_8H_6O_2NF_3$ : C, 46.9; H, 2.95; N, 6.83. Found: C, 47.0; H, 3.2; N, 7.2.

Other amide types of development precursors can be prepared in a manner similar to that illustrated in Examples 1 and 2 above, as well as by techniques which have been described in the prior art. For example, p-hydroxy-

6

acetanilide which is a useful development precursor in our invention can be prepared as described in Beilstein, vol. 13, page 460. In a similar manner, p-hydroxy- $\omega$ -chloroacetanilide can be prepared as described in Beilstein, vol. 13, first supplement, page 160. In a like manner, other substituted derivatives of aminophenols can be prepared using a mixture of free amine and acylating agent, such as those illustrated above.

The following examples will serve to illustrate the useful effects of our development precursors when incorporated within an ordinary photographic silver halide emulsion.

#### Example 3

In a manner described above, a number of oil dispersions in tricresylphosphate (10 grams of developing agent precursors in 40 grams of tricresylphosphate) were prepared. A "blank" dispersion (no developer precursor) was prepared in an identical manner to serve as a control. These dispersions were separately added to aliquot portions of an ordinary photographic gelatino-silver-bromide emulsion in the concentrations shown in the following table. The developing agent precursors are identified according to preparative example number. The table below also illustrates the useful effect obtained when a small amount of a developing agent, per se, was added to certain of the aliquot portions. These developing agents were added to the emulsions from an alcohol solution. The treated emulsion samples were separately coated on cellulose acetate supports, dried and exposed to tungsten illumination on an Eastman Type Ib Sensitometer. The coatings were then developed by treatment with an alkaline activator solution containing 1% sodium hydroxide and 5% sodium sulfite, development being effective by immersion for 15 seconds at 100° F. The relative speed for each of the coatings was measured at a point 0.3 above fog in the usual manner. The following results were obtained.

TABLE A

Coating	Addenda—Compound of Example	Rel. Speed	$\gamma$	$D_{max}$
A-1-----	None—control-----	Nil	Nil	Nil
A-2-----	p-Acetoxyphenol (0.5 mole)-----	100	.49	1.4
A-3-----	p-Acetoxyphenol (0.5 mole) plus N-methyl-p-aminophenol sulfate (4 g.)	100	0.55	1.5
A-4-----	p-Acetoxyphenol (0.5 mole) plus 1 (5.1 g.)	159	0.80	1.9

#### Example 4

Several gelatin dispersions were prepared according to the technique described in Example 3 using warm tricresylphosphate as a solvent for the development agent precursors identified in the following table. As in Example 3, a "blank" dispersion containing no development agent precursor was prepared to serve as a control. In addition, a number of compounds corresponding to the amide compounds illustrated were added to similar portions of emulsion in order to show the effect of acylation on the amino radical of such compounds.

The dispersions of development precursors or their corresponding free-amines were added to ordinary gelatino-silver-bromide emulsions at the concentration shown in Table B below. The silver halide emulsion used was a conventional gold and sulfur sensitized, high-speed emulsion which had been panchromatically sensitized. The dispersions were then coated on conventional cellulose acetate film support and dried. Each sample was then exposed on an ordinary Eastman Ib Sensitometer and processed in an ordinary alkaline activating bath, such as aqueous sodium carbonate, or an aqueous solution containing 2% sodium hydroxide and 5% sodium sulfite. Treatment was for the time indicated in the table. In addition, strips of such coatings were

developed for 5 minutes in Kodak Developer DK-50, which has the following composition:

Water, about 125° F. (50° C.)	cc	500
N-methyl-p-aminophenol sulfate	grams	2.5
Sodium sulfite, desiccated	do	30.0
Hydroquinone	do	2.5
Sodium metaborate	do	10.0
Potassium bromide	do	0.5
Water to make 1.0 liter.		

Each of the film samples was then fixed, washed and dried and the number of 0.2 log E steps read in order to determine the density obtainable with such development precursors. It is obvious from the table that the acylated compounds had a much more useful effect than the unacylated derivatives. In particular, the fog levels were much lower as evidenced by the following data:

TABLE B

Coating No.	Feature (g./Ag mole)	2' S.D. Bath		5' S.D. Bath		Fresh Tests, 5' DK-50		
		.2 log E steps	Fog	.2 log E steps	Fog	Rel. Speed	$\gamma$	Fog
(a)	Control	0	.03	0	.03	100	1.37	.11
(b)	o-Aminophenol, 20.0 g	3	.32	3	.49	Very weak		
(c)	o-(N-trifluoroacetyl)aminophenol, 20.0 g	8	.30	8	.43	15.5	1.22	.16
(d)	p-Aminophenol, 20.0 g	4	.50	5	.60	1.2	1.05	.48
(e)	p-(N-trifluoroacetyl)aminophenol, 14.1 g	10	.04	10	.07	48	0.86	.11
(f)	p-Methylaminophenol sulfate, 20.0 g	8	.50	8	.60	13.2	1.47	.24
(g)	p-(N-methyl-N-trifluoroacetyl)aminophenol, 13.95 g	11	.34	11	.40	76	1.31	.12
(h)	m-Methyl-p-(N-trifluoroacetyl)aminophenol, 20.0 g	10	.06	11	.08	85	1.23	.15
(i)	Diaminophenol.2HCl, 20.0 g	0	.80	0	.80	Heavy fog		
(j)	2,4-(N,N-trifluoroacetyl)diaminophenol, 20.0 g	4	.15	6	.46	18	1.40	.20

While the above data were obtained using freshly coated films, the useful effects of our development precursors are even more apparent when the coatings are incubated under accelerated conditions to simulate storage conditions, such as might be encountered in actual commercial handling of a film. This effect can be seen from the following data:

TABLE C

Coating No.*	Fresh Tests, 5' DK-50			1 Week Incubations, 120° F., 5' DK-50		
	Relative Speed	$\gamma$	Fog	Relative Speed	$\gamma$	Fog
(a)	100	1.37	0.11	78.0	1.16	0.20
(b)	Very weak image			Very weak image		
(c)	15.5	1.22	0.16	13.0	1.30	0.17
(d)	1.2	1.05	0.48	1.0	1.10	0.48
(e)	48.0	0.86	0.11	53.0	1.21	0.16
(f)	13.2	1.47	0.24	17.2	1.37	0.21
(g)	76.0	1.31	0.12	73.0	1.20	0.17
(h)	85.0	1.23	0.15	83.0	1.18	0.18
(i)	Heavy fog			Very heavy fog		
(j)	18.0	1.40	0.20	15.0	1.36	0.20

\*Nos. correspond to those of Table B.

## Example 5

In a manner similar to that described in Example 3, p-hydroxy- $\omega$ -chloroacetanilide was incorporated in an ordinary, high-speed, gelatino-silver-bromiodide emulsion at the concentrations indicated in the following table. An aliquot portion of emulsion was treated with a "blank" dispersion as described above for purposes of comparison. The emulsions were then coated and processed as described in Example 3, the following data being obtained:

TABLE D

Coating No.	Feature (g./Ag mole)	2' S.D. Bath		5' S.D. Bath		Fresh Tests, 5' DK-50		
		.2 log E steps	Fog	.2 log E steps	Fog	Rel. Speed	$\gamma$	Fog
(a)	Control	0	.05	0	.05	100	1.35	.12
(b)	Chloroamide, 20 g	7	.05	11	.06	89	1.28	.09
(c)	Chloroamide, 40 g	12	.06	13	.07	85	1.23	.09

In a manner similar to that illustrated above, it was found that p-hydroxy- $\beta$ -chloropropionanilide could be used effectively as a development precursor in photographic silver halide emulsions. In like manner, it was found that p-hydroxy- $\omega$ -bromoacetanilide could also be effectively used as a development precursor.

As shown above, it has been found that the development precursor compounds of our invention are particularly useful in that emulsions containing them are considerably more stable than emulsions containing developing compounds, per se. This advantage becomes particularly apparent upon incubation at elevated temperatures for extended periods of time. For example, hydroquinone and p-aminophenol have the effect of lowering the speed of the emulsions if either is incorporated within the emulsion as an active developing agent. While

the disadvantages of using such incorporated developing agents can be mitigated somewhat by incorporating the developing agent in a separate, contiguous layer, the development precursors of the present invention make this step unnecessary. However, the development precursors of our invention can likewise be used to advantage by incorporation in a layer contiguous to the emulsion layer.

The developer precursors of our invention can be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the non-image 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 Yackel et al. 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 Canadian Patent 602,607, issued August 2, 1960. They may also be used in emulsions intended for use in a monobath process

9

such as described in Haist et al. U.S. Patent 2,875,048, issued February 24, 1959, and in web-type processes, such as the one described in Tregillus et al. U.S. patent application Serial No. 835,473, filed August 24, 1959, now U.S. Patent No. 3,179,517.

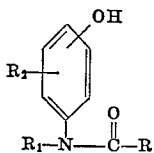
Of course, the activator solutions which are used in our invention are stable for extended periods of time and are not subject to the harmful decomposition reactions so common to conventional photographic developing solutions when these developing solutions are stored for extended periods of time. No special precautions are required to prevent oxidation of the activator solutions since they are inherently quite stable. If desired, the activator solutions can be incorporated in a carrier, such as gelatin and coated in contact with the photographic silver halide emulsion layer which contains the development precursors of our invention. After exposure, the development can be effected merely by heating the photographic emulsion layer to a temperature sufficient to release water, which may be present in the support or in a separate layer in the photographic element. This water then dissolves the activator solution from the hydrophilic colloid layers and takes it into the photographic halide emulsion layer where the emulsion is effected.

The elevated temperatures from about 95–150° C. are usually sufficient to effect development in this manner. If desired, additional moisture can be added by spraying steam upon the sensitive surface of the photographic element.

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 and a photographic silver halide emulsion layer, and integral with said photographic element a water-permeable, hydrophilic colloid containing a silver halide development precursor represented by the following general formula:



wherein R represents a member selected from the class consisting of an alkyl group and a halogenoalkyl group, R<sub>1</sub> represents a member selected from the class consisting of a hydrogen atom and an alkyl group, and R<sub>2</sub> represents a member selected from the class consisting of a hydrogen atom, an alkyl group, a halogen atom, an alkoxy group, an acylamido group and an acyloxy group.

2. A photographic element as defined in claim 1 wherein said precursor is incorporated in said silver halide emulsion layer.

3. A photographic element as defined in claim 1 wherein said precursor is incorporated in a hydrophilic colloid layer contiguous to said silver halide emulsion layer.

4. A photographic element as defined in claim 1 wherein said precursor is incorporated in said photographic element as a dispersion in a water-insoluble, crystalloidal solvent.

5. A photographic element as defined in claim 1 wherein said precursor is o-(N-trifluoroacetyl)aminophenol.

6. A photographic element as defined in claim 1

10

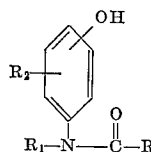
wherein said precursor is p-(N-trifluoroacetyl)aminophenol.

7. A photographic element as defined in claim 1 wherein said precursor is p-(N-methyl-N-trifluoroacetyl)aminophenol.

8. A photographic element as defined in claim 1 wherein said precursor is m-methyl-p-(N-trifluoroacetyl)aminophenol.

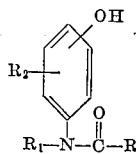
9. A photographic element as defined in claim 1 wherein said precursor is 2,4-(N,N-trifluoroacetyl)diaminophenol.

10. A photographic element comprising a support and a photographic silver halide emulsion layer, and integral with said photographic element a water-permeable, hydrophilic colloid containing a development precursor represented by the following general formula:



wherein R represents a member selected from the class consisting of an alkyl group and a halogenoalkyl group, R<sub>1</sub> represents a member selected from the class consisting of a hydrogen atom and an alkyl group, and R<sub>2</sub> represents a member selected from the class consisting of a hydrogen atom, an alkyl group, a halogen atom, an alkoxy group, an acylamido group and an acyloxy group, said photographic element containing in addition to said development precursor a 3-pyrazolidone photographic silver halide developing agent.

11. A photographic element comprising a support and a photographic silver halide emulsion layer, and integral with said photographic element a water-permeable, hydrophilic colloid containing a development precursor represented by the following general formula:



wherein R represents a member selected from the class consisting of an alkyl group and a halogenoalkyl group, R<sub>1</sub> represents a member selected from the class consisting of a hydrogen atom and an alkyl group, and R<sub>2</sub> represents a member selected from the class consisting of a hydrogen atom, an alkyl group, a halogen atom, an alkoxy group, an acylamido group and an acyloxy group, said photographic element containing in addition to said development precursor a hydroquinone silver halide developing agent precursor, at least one of whose hydroxyl radicals has been esterified to form an ester hydrolyzable in aqueous alkaline solution.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

1,497,252	6/1924	Theimer	260—562
1,853,455	4/1932	Reddelien et al.	96—66
2,653,158	9/1953	Young et al.	260—562
2,751,295	6/1956	Salminen et al.	96—95
3,113,026	12/1963	Sprung	96—66

NORMAN G. TORCHIN, *Primary Examiner*,

J. TRAVIS BROWN, *Examiner*.