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3,794,488

PHOTOSENSITIVE AND THERMOSENSITIVE ELEMENT, COMPOSITION AND PROCESS

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ABSTRACT OF THE DISCLOSURE

Amidoximes are active developing agents for photographic silver salts in strongly alkaline solutions. They may be incorporated in silver halide emulsions and they can be activated by immersion in alkali or by application of heat. They may be used in chemical or physical development; such as, diffusion transfer processing.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to certain amidoxime photographic silver salt developing agents and to photographic elements, processing compositions, and to processes employing developer compositions containing certain amidoxime silver halide developing agents. In another of its aspects, it relates to a method of developing a latent image in a photographic element employing the described amidoxime silver halide developing agents.

Description of the prior art

It is well known to develop a latent image in a photographic silver halide element using a silver halide developing agent. Developing agents for this purpose have included for example, aminophenol developing agents and polyhydroxybenzene developing agents. This is described, for example, in The Theory of the Photographic Process by Mees and James, 3rd ed., 1966, pp. 278–311.

It has been desirable to provide developing agents which are sufficiently active to provide desired sensitometric properties within the shortest development time and also result in colorless or low-colored oxidation products. Developing agents which provide colorless or low-colored oxidation products are especially desirable in photographic systems in which the oxidation products are not to be removed from the system, such as in systems in which usual washing with water is avoided.

It is, furthermore, desirable to find developing agents that can advantageously be employed in a variety of photographic products, for example, in photographic developer and processing solutions, as incorporated developing agents in photographic emulsions, in photographic products that may be processed according to the so-called "dry processing" techniques, in photographic diffusion transfer products, etc.

Developing agents having such universal applications are unusual. A developing agent, for example, which is desirably employed in a developing solution can be useless as an incorporated developing agent, i.e., the developing agent may not be stable in the emulsion. A developing agent, as incorporated, may cause spontaneous reduction (fogging) or may be lost by oxidation. A developing agent which is incorporated in a photographic element adapted for "wet processing" may not be desirable for incorporation in a photographic element adapted for "dry processing" since most developing agents have a tendency to induce staining unless washed out from the elements upon processing.

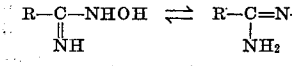
There is a continuing need for compounds which can develop not only exposed photographic silver halide, but

additionally other photographic silver salts to visible images. The developing action should be reasonably fast and should produce images evidencing strong image discrimination with little propensity of staining.

Use of hydroxamic acids, such as, benzohydroxamic acid in developing solutions and/or silver halide emulsions is known, but these hydroxamic acids are employed as supplemental developers or in a non-developing function, and not as a principle developing agent. Schestakoff U.S. Pat. 1,663,959, issued Mar. 27, 1928, for example, describes the use of benzohydroxamic acid as an auxiliary developer in combination with an ordinary developer.

SUMMARY OF THE INVENTION

It has been unexpectedly discovered that the amidoximes can be employed as effective developing agents in a wide variety of photographic materials, as described herein. In accordance with the invention, photographic silver salt developing compositions are provided which employ amidoximes having the general formula:



where R may be H, alkyl having 1–12 carbon atoms, aryl having 6 to 12 carbon atoms or heterocyclic having 6 to 12 carbon atoms.

The activity of such developing agent in many photographic products is unexpected and unobvious since the oximes are not active silver halide developing agents.

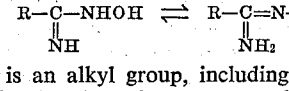
An object of this invention is to provide active developing agents. A further object is ot provide developing agents having low-colored oxidation products. A further object is to provide developing agents which can be incorporated in a photographic emulsion without undesirable oxidation of the agents or fogging of the emulsion. A further object is to produce photographic emulsions which may be processed by the application of heat.

Another object of this invention is to provide photographic silver salt developing agents capable of providing increased speeds and strong image discrimination.

A further object of this invention is to provide photographic silver salt processing composition which provide desired sensitometric properties and developing action wtihout objectionable stain.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The amidoximes particularly useful in the invention have the general structural formula:



wherein R is an alkyl group, including substituted alkyl groups having 1 to 12 carbon atoms, such as methyl, ethyl, propyl, butyl, alicyclic substituted alkyl such as cyclopentylethyl, hydroxyalkyl such as hydroxyethyl, hydroxypropyl, tris(hydroxymethyl)butyl, carboxyalkyl such as carboxymethyl, carboxyethyl, carboxyphenyl, unsaturated hydrocarbons, including substituted unsaturated hydrocarbons such as vinyl allyl, phenylallyl, alicyclic such as cyclophentyl, methylcyclopentyl, cyclohexyl, cyclohexylbromide, cyclohexenyl, and the like; an aryl group including substituted aryl groups, and having 6 to 12 carbon atoms, as exemplified by phenyl, naphthyl, alkaryl, such as xylyl, mesityl, ethylphenyl, propylphenyl, halide substituted phenyl such as bromophenyl, dichlorophenyl, carboxyphenyl and the like; and a heterocyclic group having 5 or 6 atoms, e.g. 2-furyl, thienyl, benzothienyl, pyridyl, quinolyl, and the like. In a preferred aspect of this invention, R represents the atoms necessary to complete a 5 or 6 member heterocyclic ring, preferably containing one hetero atom such as N or S, the selection of

the amidoxime being within the skill of the practitioner in the art.

Illustrative, examples of amidoximes which may be employed according to the invention are:

p-tolyl amidoxime
p-bromophenyl amidoxime
p-xylyl amidoxime
m-carboxyphenyl amidoxime
2-thienyl amidoxime
methyl amidoxime
3,4-dichlorophenyl amidoxime
2,5-dichlorophenyl amidoxime
p-methoxyphenyl amidoxime
p-chlorophenyl amidoxime.

A significant feature and advantage of the amidoxime developing agents is its substantially low propensity for staining, hence the developing agents need not be washed from the emulsion following processing. This feature is particularly advantageous in rapid machine processing and in photographic elements adapted for dry processing. A second significant feature and advantage is the increase in developing rate obtained when the amidoximes are employed in combination with pyrazolidone silver halide developing agents. This aspect of the invention is illustrated by Example 3 which follows.

When used in such combination, the mole ratio of amidoxime to pyrazolidone developing agent may vary over a wide range. The selection of the ratio is within the skill of the practitioner in the art. The selection of ratios can depend on a number of factors such as the type of photographic system being developed, the method of development, whether the developer combination is incorporated or part of a developer or processing solution or package. A useful mole ratio of amidoxime to pyrazolidone developing agent is 100:1 to about 0.5:1. A preferred ratio is 20:1 to 5:1. A particularly useful ratio is 10:1 on a molar basis.

Another significant feature of the developing agents of the present invention is their substantial stability when incorporated in a photographic element. They neither cause nor induce spontaneous reduction, nor are the developing agents lost by oxidation; hence the shelf life of a photographic product is substantially extended.

The developing agents of this invention can be suitably utilized in any of a variety of locations with respect to a photographic system. They can be employed in photographic processing and/or developing solutions, for example, in an aqueous alkaline developer composition. They can be incorporated into a layer of a photographic element such as a silver halide emulsion layer, an overcoat layer or an interlayer of a photographic element. They can be utilized in a developer composition intended for use in a diffusion transfer process or they can be utilized in one or more layers of a photographic element employed in a diffusion transfer process.

Diffusion transfer processes and photographic elements in which the developing agents are useful are described, for example, in U.S. Pats. 2,352,014 of Rott issued June 20, 1944; 2,543,181 of Land issued Feb. 27, 1951; and 3,337,342 of Green issued Aug. 22, 1967. The developing agents of this invention can also be employed in so-called high-speed diffusion transfer processes as described, for example, in U.S. Pat. 3,326,683 of Land et al. issued June 20, 1967; or in other types of diffusion transfer processes such as those described in U.S. Pats. 2,857,274 of Land et al. issued Oct. 21, 1958; 3,020,155 of Yackel et al, issued Feb. 6, 1962; 2,584,030 of Land issued Jan. 29, 1952; and 2,923,623 of Land issued Feb. 2, 1960. These patents describe typical photographic products suitable for diffusion transfer systems comprising a combination of (a) a photosensitive element which comprises a support having thereon at least one photosensitive silver salt emulsion layer (b) an image-receiving layer, and (c) a rupturable container containing an alkaline processing composition comprising a silver halide developing agent, and typically a silver halide solvent.

The amidoximes can be located in the photosensitive emulsion layer or in contiguous layers of a photographic element and a pyrazolidone developing agent located in the activator solution or layer. The latter arrangement is especially desirable since it allows for the most optimum keeping conditions. Hence in a preferred embodiment there is provided a photographic element comprising a support having thereon at least one photographic silver salt emulsion layer containing an amidoxime described herein; and an activator layer or solution containing 1-phenyl-3-pyrazolidone. The developing agents of this invention can be utilized in combination with photosensitive elements which are adapted for processing by the so-called "dry photography" (heat) development methods. No liquids, vapor or other processing aids need be employed in order to obtain a high image density or desirable image tone in the photosensitive element having incorporated therein the developers of this invention. Dry photography processes are described, for example, in U.S. Pats. 3,457,075 of Morgan et al. issued July 22, 1969; 3,152,903 of Sheppard et al. issued Oct. 13, 1964 or 3,152,904 of Sorensen et al. issued Oct. 13, 1964.

Photographic silver halide emulsion, preparations, addenda, processing and systems can be used as disclosed in Product Licensing Index, vol. 92, December 1971, publication 9232, pp. 107–110, paragraphs I–XI, XIII and XXIV.

Suitable silver halide developing agents which can be employed with the developing agents of the invention include, for example, polyhydroxybenzenes, such as hydroquinone developing agents, e.g., hydroquinone; alkyl substituted hydroquinones such as t-butylhydroquinone, methylhydroquinone and 2,5-dimethyl hydroquinone; catechols and pyrogallol; halogen substituted hydroquinones such as chlorohydroquinone or dichlorohydroquinone; alkoxy substituted hydroquinones such as methoxy hydroquinone 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)hydroxyamine; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone, including those described in British Pat. 930,572; an acyl derivative of p-aminophenol such as described in British Pat. 1,045,303; ascorbic acid; hydroxytetronic acid and hydroxytetronimide developing agents; reductone developing agents such as anhydrodihydropyrrolidino hexose reductone and the like.

The photographic developer compositions can include ingredients commonly employed for processing photographic elements in addition to the developing agents, e.g., stabilizer compositions, activator compositions, hardener compositions and the like.

The photographic developer compositions according to the invention can contain a silver halide solvent. A variety of silver halide solvents are suitable, such as alkali metal and ammonium thiocyanates, e.g., sodium and potassium thiocyanate and ammonium thiocyanate, alkali metal thiosulfates, such as sodium thiosulfate and potassium thiosulfate, thiourea compounds, and the like.

Any alkaline developer activator can be employed to activate the developing agents of the invention in non-dry processing photographic processes so long as the activators provide the desired pH. These include those commonly employed in the photographic are as development activators, such as inorganic alkali, e.g., alkali metal hydroxide including sodium hydroxide, potassium hydroxide and lithium hydroxide, alkali metal carbonate, such as sodium carbonate, sodium bicarbonate, fuming ammonia, and the like as well as organic alkali such as organic amines and aminoalkanols, e.g., ethanol amines and aminodiethanolamine or morpholine. The concentration of development activator can vary depending on the various components of the system, the photographic

emulsion employed, the desired image, and the like. A concentration is usually employed which provides a pH of at least about 8, typically from about 10 to about 14, and preferably about 12 to about 14.

In another embodiment of the invention photosensitive elements are provided, said elements comprising a support, at least one silver salt layer and incorporated in said element, a photographic silver salt developing agent of this invention. The developer can be employed in a photographic silver salt emulsion layer, an overcoat layer, a layer under the emulsion layer, or virtually any of the layers contiguous to the silver salt to be developed.

The developing agents of the invention can be employed in photographic elements designed for processing in stabilization type processing. For example, they can be incorporated in one or more layers of a photographic element which is exposed, activated by contact with alkaline activator, and then contacted with a thiocyanate or thiosulfate solution, such as an ammonium thiocyanate, or they can be incorporated in the alkaline activator. Such processes are described, for example, in U.S. Pat. 3,326,-864 of Nishio issued June 20, 1967; British Pat. 1,004,302; French Pat. 1,516,556 of Fassbender; and in an article by H. D. Russell, E. C. Yackel and E. G. Grouse in the PSA Journal, August 1950, pp. 59–62, entitled "Stabilization Processing of Films and Papers."

The developing agents of this invention as described herein can be used in layers of photographic elements or processing solutions intended for use in monobath processing such as described in U.S. Pat. 2,875,048 of Haist et al. issued Feb. 24, 1959, and British Pat. 1,063,844 of Beavers et al., issued Mar. 30, 1967, and in web-type processing, such as described in U.S. Pat. 3,179,517 of Tregillus et al. issued Apr. 20, 1965.

The developing agents of this invention can be employed in a photographic silver salt emulsion designed for diffusion transfer processing and/or in a developer composition designed for developing and stabilizing the element. A typical developer composition is disclosed in U.S. Pat. 3,120,795 of Land et al. issued Feb. 11, 1964.

Hence, in accordance with an aspect of the invention there is accordingly provided in combination (a) a photographic element comprising a photographic silver salt layer, (b) a viscous processing composition, within a releasing means, e.g., a rupturable container, comprising:

(i) a silver halide solvent,
(ii) an alkaline development activator,
(iii) optionally, a 3-pyrazolidone developing agent, a diaminophenol developing agent or other auxiliary developing agent described herein, and
(iv) the novel developing agent of this invention, and
(c) an image receiving layer comprising development nuclei, especially palladium development nuclei, dispersed in a polymeric binder.

Albeit the developing agent is generally located in a releasing means, it can be suitably employed in a variety of locations with regard to a diffusion transfer system. The novel developer can be provided in the silver salt layer or emulsion, in a layer near to the silver salt layer, in the image receiving layer containing silver precipitating nuclei or development nuclei as well as in the rupturable container.

In accordance with a typical diffusion transfer process a photographic element is exposed imagewise, the exposed silver halide is developed at a pH above 8, typically above 10 and preferably at a pH of about 12 to about 14, in the presence of the novel developer. The unexposed silver salts in the photosensitive silver salt layer is contacted with a silver halide solvent to form an imagewise distribution of a silver complex in the unexposed areas of said photographic silver salt layer; and at least part of the silver complex is transferred to an image receiver layer containing development nuclei, contiguous to the photosensitive layer, thereby forming a visible image on said receiver layer.

Processing conditions, time of development, and the like can vary depending on the desired image, the particular components of the described element, processing composition, and image receiver. Typically processing is carried out under normal atmospheric conditions and is completed within about 60 seconds, and preferably, within about 10 seconds.

Usually the silver halide solvent will be sodium thiosulfate; however, various organic silver halide complexing agents such as those described by Haist et al., Phot. Sci. Eng., 5, 198 (1961) and in Kodak French Pat. 1,312,687 issued Nov. 12, 1962, and Belgian Pat. 606,559 of Ulrich et al., issued July 26, 1960, and similar agents can also be used.

The light-sensitive element, receiving element or processing composition can also contain toning agents such as, for example, polyvalent inorganic salts of the type described in U.S. Pat. 2,698,236 of Land issued Dec. 28, 1954, silica as described in U.S. Pat. 2,698,237 of Land issued Dec. 28, 1954, and heterocyclic mercaptans such as the mercapto azoles, e.g., mercapto diazoles, mercapto triazoles and mercapto tetrazoles.

Typically, the developing agent is provided in a viscous liquid photographic developer composition comprising (a) a silver halide solvent, and (b) the silver halide developing agent of the invention. The viscous liquid photographic developer composition can also contain additional silver halide developing agents, as described herein, especially a 3-pyrazolidone silver halide developing agent.

A viscous liquid photographic developer composition can comprise a viscous monobath. Suitable viscous monobaths are described, for example, in the Monobath Manual, by Grant M. Haist (1966), Morgan and Morgan, Inc., Hastings On Hudson, N.Y.

Typically, a suitable developer composition according to the invention can comprise a viscous developer containing:

(a) a silver halide solvent, such as sodium thiosulfate,
(b) a diaminophenol auxiliary developing agent, such as 6-methoxy-2,4-diaminophenol or 6-ethyl-2,4-diaminophenol or a 3-pyrazolidone auxiliary developing agent such as 1-phenyl-3-pyrazolidone or 1-phenyl-4,4-dimethyl-3-pyrazolidone,
(c) the developing agent of the invention,
(d) an alkaline development activator, and
(e) a thickening agent, such as a cellulose derivative, e.g., hydroxyethyl cellulose and/or carboxymethyl cellulose.

Suitable viscosities for the viscous composition can vary over a wide range. The viscosity is usually from about 20 to about 1000 cps. Various thickening agents are suitably employed in the described processing compositions and processes of the invention. Any of those commonly employed in diffusion transfer photographic systems can be employed. These include those described in the art, such as cellulose derivatives, e.g., hydroxyethyl cellulose and/or carboxymethyl cellulose.

In another aspect of this invention, it has been discovered that the developing agents described herein can be utilized in the photographic process generally referred to as "dry photography." The elements employed in dry photography are photosensitive, i.e., a latent image is formed imagewise in the exposed areas of a silver salt layer, and thermosensitive, i.e., substantially permanent, visible images of photographic sharpness and high visual contrast can be produced often within seconds through the mere application of heat. The dry photographic elements are developed by heating to within a temperature range of from about 80° C. to about 250° C.

Typically a "dry photographic" element comprises a support having thereon an oxidation-reduction image forming combination said combination comprising a silver salt, preferably an organic silver salt, and a reducing

agent, and a catalyst for the oxidation-reduction image forming combination.

In accordance with an aspect of the invention, the amidoximes either as the developing agent or in combination with an auxiliary developing agent such as a pyrazolidone can be employed as the reducing agent or composition in the "dry photographic" element.

Other reducing agents as described herein can be employed in combination with the developing agents of this invention, and include, for example, the prior art silver halide developing agents and/or substituted phenols and napthols described in De Mauriac, Belgian Pat. 766,589 issued June 15, 1971.

As the oxidizing agent, of the oxidizing-reduction image forming combination, a silver salt of an organic acid is preferably employed. The silver salt of the organic acid should be resistant to darkening under illumination to prevent undesired deterioration of a developed image. An especially suitable class of silver salts of organic acids is the water insoluble silver salts of long-chain fatty acids which are stable to light. Typically, the silver salts include silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caprate, silver myristate, and silver palmitate. Other suitable oxidizing agents are silver benzoate, silver phthalazinone, silver benzotriazole, silver saccharin, silver 4'-n-octadecyloxy-diphenyl-4-carboxylic acid, silver orthoamino-benzoate, silver acetamidobenzoate, silver furoate, silver comphorate, silver p-phenylbenzoate, silver phenyl acetate, silver salicylate, silver butyrate, silver terephthalate, silver phthalate, silver acetate, and silver acid phthalate. Nonsilver salts can be employed as oxidizing agents, such as zinc oxide, gold stearate, mercuric behenate, auric behenate and the like, however, silver salts are generally preferred.

Typically, a photosensitive salt is present in the "dry photographic" elements in minor or catalytic amounts. A suitable concentration range of the catalyst is generally from about 0.01 to about 0.50 mole of photosensitive silver salt per mole of oxidizing agent. Suitable silver salts include photosensitive silver halides, e.g., silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, or mixtures thereof.

The "dry photographic" elements preferably contain an activator-toning agent. Suitable activator-toning agents which can be employed include cyclic imides such as:

Phthalimide,
N-hydroxyphthalimide,
N-potassium phthalimide,
N-mercury phthalimide,
Succinimide, and
N-hydroxysuccinimide.

Other activator-toning agents can be employed in combination with or in place or the cyclic imides. Such other activator-toning agents are generally heterocyclic compounds containing at least two hetero atoms in the heterocyclic ring, at least one being nitrogen. Illustrative compounds include phthalazinone, phthalic anhydride, 2-acetylphthalazinone and 2-phthalylphthalazinone. Grant U.S. Pat. 3,080,254 issued Mar. 5, 1963, and Workman U.S. Pat. 3,446,648 issued May 27, 1969, describe suitable activator-toning agents.

Activator-toning agents are suitably employed at a concentration of about 0.10 mole to about 1.05 moles per mole of oxidizing agent, however, lower and higher concentrations can be employed.

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

EXAMPLE 1

Preparation of compounds

Compounds given in Table I are prepared according to modification of the general procedure given in Chemical Reviews, 62, 157 (1962). In our method, a slurry of hydroxylamine hydrochloride in methanol is treated with an equivalent of sodium methoxide in methanol, keeping the temperature below 15° C. Sodium chloride is filtered off and washed with a small amount of methanol. The corresponding nitrile is added to the filtrate. This reaction mixture is kept at room temperature for 1–2 days. It is then concentrated, and the precipitated amidoxime filtered off and recrystallized.

The preparation of formamidoxime is taken from J. Barrows, Chemical Abstracts, 60:12004e (1964).

TABLE I

Dry physical development with R—C(=NH)NHOH

Compound No.	R	Time (sec.)	Image density
1	H—	3	High.
2	CH_3—	2	Good.
3	C_2H_5—	2	High.
4	n-C_3H_7—	3	Do.
5	$ClCH_2$—	2	Good.
6	HOC_2H_4—	3	High.
7	C_6H_5—	4	Good.
8	p-ClC_6H_4—	3	Do.
9	p-HOC_6H_4—	7	Do.
10	p-CH_3O-C_6H_4—	2	Do.
11	p-HOOC—C_6H_4—	10	Fair.
12	p-NO_2—C_6H_4—	3	Good.
13	m-NO_2—C_6H_4—	3	Do.
14	γ-pyridy	5	Do.
15	β-pyridy	4	Do.
16	2-thienyl	3	Do.
17	—CH_2—C(=NH)NHOH	5	Fair.
18	—C_4H_8—C(=NH)NHOH	3	High.
19	—C_2H_4—S—C_2H_4—C(=NH)NHOH	4	Good.
20	p-C_6H_4—C(=NH)NHOH	4	Do.
21	p-C_6H_4—O—C_6H_4—C(=NH)NHOH	3	High.
22	—$CH_2N(CH_2C(=NH)NHOH)_2$	----------	

EXAMPLE 2

Use in dry physical development systems

A mixture of silver behenate and behenic acid as described in U.S. Pat. 3,457,075 of Morgan et al. issued July 22, 1969, is prepared by precipitation with silver nitrate from a solution of sodium behenate and behenic acid in non-polar solvent. The precipitate is thoroughly washed and dried.

A coating composition is prepared by mixing the following components:

Silver behenate	g	42.0
Behenic acid	g	32.0
Polyvinyl butyral	g	15.0
Acetone-toluene (1:1 parts by volume)	ml	500

After ball-milling for about 18 hours, 75.0 ml. of an acetone solution containing 1 perecnt by weight of lithium bromide is added to the above dispersion and the mixture is stirred situ. The resulting dispersion is coated on a paper support at a wet thickness of 0.006 in. The resulting coating is dried.

Various amidoximes as described in Table I are dissolved in an acetone methyl alcohol solution to provide a 0.02 molar concentration. The solution is then spotted on to the described photosensitive element with a glass stirring rod and dried. No activator-toning agent is added to the composition. The coating is dried and then exposed imagewise to light. The element is then heated on a mandrel to 140° C. As will be seen in Table I, strong images are obtained in times of from 2 to 10 seconds. The images are generally black in hue and no auxiliary toning or accelerating agent is necessary. In contrast, hydroxylamine sulfate, an agent of the prior art, produces almost no image under these test conditions.

EXAMPLE 3

Dry physical development in presence of toning agent

A coating similar to that of Example 2 is employed except that the coating also contains phthalazinone, the chemical commonly employed in the art as a toner-ac-

celerator. 0.02 molar solutions of the developing agents in acetone and methyl alcohol are coated onto the surface of this emulsion and allowed to dry. The emulsion is then exposed to light behind a suitable graphic test object and processed at 115° C. Strong images with low fog are obtained in times of 6 to 15 seconds as indicated in Table II. Most of these compounds give neutral image tones and clear, fog-free backgrounds.

TABLE II.—DEVELOPMENT WITH PHTHALAZINONE 115° C.

Compound No.	Time, (sec.)	Density of— Image	Fog	Image tone
1	8	Good	Low	Brown.
2	15	Fair	None	Do.
6	15	Good	Fair	Orange.
7	6	do	None	Neutral.
8	15	Fair	do	Do.
9	12	Good	do	Do.
11	15	Fair	do	Warm black.
14	15	do	do	Do.
16	15	Good	do	Neutral.
19	8	do	do	Do.
20	15	Fair	do	Warm black.
21	15	do	do	Neutral.

EXAMPLE 4

Use for aqueous development

Various amidoximes, as listed in Table II, are employed in a solution containing 0.02 molar concentrations of the developing agents, 0.2 molar sodium sulfite and 0.5 molar sodium hydroxide.

TABLE III.—DEVELOPMENT IN AQUEOUS SOLUTION

Compound No.	Time, min.	Density of— Image	Fog
7	32	1.74	0.10
8	32	1.22	0.04
10	32	2.65	0.18

A fine grain bromoiodide emulsion is exposed to a step wedge and developed in each solution for a series of times at 68° F. Although the compounds do not develop rapidly, images of good density and low fog are produced on prolonged development. This test is repeated, except the solution is modified by the addition of .002 molar 1-phenyl-3-pyrazolidone. The activity of the developer is very greatly increased as is shown in Table IV. This illustrates that the amidoximes of our invention can be advantageously combined with other developers. In this case strong superadditive development is obtained.

TABLE IV.—MIXTURES WITH 1-PHENYL-3-PYRAZOLIDONE

Compound No.	Time, min.	Density of— Image	Fog
7	5.5	2.00	0.10
8	6.0	2.00	0.04
10	4.2	2.00	0.18

EXAMPLE 5

Freedom from staining propensity

Alkaline solutions of various amidoximes of our invention are exposed to the air. Even in the presence of sodium hydroxide they remain colorless or show only a light tint. In contrast, hydroquinone and p-aminophenol, agents of the prior art, oxidize to deeply colored solutions. Similarly, alkaline solutions of the amidoximes of our invention left in processed paper give no stain, while alkaline solutions of hydroquinone and paraminophenol produce deep stain.

The image density values given above are represented as follows:

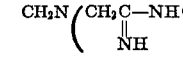
Low-reflectance density under 0.3
Fair-reflectance density 0.3–0.8
Good-reflectance density over 0.8.

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

We claim:

1. A photographic processing composition comprising an alkaline development activator, and an amidoxime silver salt developing agent, wherein said amidoxime is represented by the structural formula:

wherein R is H, a heterocyclic group having 5 or 6 atoms, CH_3, C_2H_5, n-C_3H_7, $ClCH_2$, HOC_2H_4, C_6H_5, p-ClC_6H_4, p-HOC_6H_4, p-CH_3O—C_6H_4, p-HOOC—C_6H_4, p-NO_2—C_6H_4, m-NO_2—C_6H_4, γ-pyridyl, β-pyridyl, 2-thienyl, CH_2—C(=NH)NHOH, C_4H_8—C(=NH)NHOH, C_2H_4—S—C_2H_4—C(=NH)NHOH, p-C_6H_4—C(=NH)NHOH, p-C_6H_4—O—C_6H_4—C(=NH)NHOH or



2. A photographic composition of claim 1 which also contains a silver halide solvent.

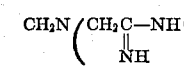
3. A photographic processing composition of claim 1 which also contains a pyrazolidone auxiliary silver halide developing agent.

4. A photographic composition of claim 3 wherein the mole ratio of the amidoxime to pyrazolidone is in the range of from about 20:1 to about 5:1.

5. A photographic element comprising a support having thereon at least one photographic silver halide layer and incorporated in said element as a silver halide developing agent, an amidoxime represented by the structural formula:



wherein R is H, a heterocyclic group having 5 or 6 atoms, CH_3, C_2H_5, n-C_3H_7, $ClCH_2$, HOC_2H_4, C_6H_5, p-ClC_6H_4, p-HOC_6H_4, p-CH_3O—C_6H_4, p-HOOC—C_6H_4, p-$NO_2C_6H_4$, m-NO_2—C_6H_4, γ-pyridyl, β-pyridyl, 2-thienyl, CH_2—C(=NH)NHOH, C_4H_8—C(=NH)NHOH, C_2H_4—S—, C_2H_4—C(=NH)NHOH, p-C_6H_4—C(=NH)NHOH, p-C_6H_4—O—C_6H_4—C(=NH)NHOH or



6. A photographic element of claim 5 which also includes a pyrazolidone developing agent.

7. A photographic element of claim 5 wherein said developing agent is present in said silver halide emulsion layer.

8. A photographic element as in claim 5 wherein said developing agent is in a layer contiguous to said silver halide layer.

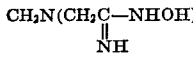
9. A photographic element as in claim 5 wherein said amidoxime is located in said silver halide emulsion layer and a pyrazolidone developing agent is in a layer contiguous to said silver halide layer.

10. A process of developing an exposed photographic element, said element comprising a support having thereon at least one photographic silver halide layer, said process comprising contacting said exposed element with an amidoxime developing agent represented by the structural formula:



wherein R is H, a heterocyclic group having 5 or 6 atoms,

CH_3, C_2H_5, n-C_3H_7, $ClCH_2$, HOC_2H_4, C_6H_5, p-ClC_6H_4, p-HOC_6H_4, p-CH_3O—C_6H_4, p-HOOC—C_6H_4, p-NO_2—C_6H_4, m-NO_2—C_6H_4, γ-pyridyl, β-pyridyl, 2-thienyl, CH_2—C(=NH)NHOH, C_4H_8—C(=NH)NHOH, C_2H_4—S—C_2H_4—C(=NH)NHOH, p-C_6H_4—C(=NH)NHOH, p-C_6H_4—O—C_6H_4—C(=NH)NHOH or



11. A process of developing an exposed photographic element of claim **5** wherein the amidoxime developing agent is activated by heating the photographic element.

12. A process of developing an exposed photographic element of claim **5** wherein the amidoxime developing agent is activated by contacting said element with an alkaline activator.

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96—48 PD, UX, 66 R, 66 T, 76 XR, 95, 114.1 UX