United States Patent [19]

Wilson et al.

[11] **3,751,255**

[45] **Aug. 7, 1973**

[54] **PHOTOSENSITIVE AND THERMOSENSITIVE ELEMENT, COMPOSITION AND PROCESS**

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[22] Filed: **Mar. 24, 1972**

[21] Appl. No.: **237,933**

[52] **U.S. Cl.** ..... **96/66 R,** 96/29 R, 96/29 L, 96/66.3, 96/76 R, 96/88, 96/95, 96/114.1

[51] **Int. Cl.** **G03c 5/00,** G03c 5/30, G03c 1/42

[58] **Field of Search** ..... 96/66.5, 95, 114.1, 96/66.3, 76 R, 66 R

[56] **References Cited**

UNITED STATES PATENTS

853,643	5/1907	Lumiere & Lumiere	96/95
3,179,517	4/1965	Tregillus et al.	96/29 R

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[57] **ABSTRACT**

Sulfhydroxamic acids are active developing agents for photographic silver salts in strongly alkaline solutions. They form super additive mixtures with other silver halide developing agents. 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 in diffusion transfer processing.

19 Claims, No Drawings

PHOTOSENSITIVE AND THERMOSENSITIVE ELEMENT, COMPOSITION AND PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to certain sulfhydroxamic acid photographic silver salt developing agents and to photographic elements, processing compositions, and to processes employing developer compositions containing certain sulfhydroxamic acid 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 sulfhydroxamic acid silver halide developing agents.

2. 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 Edition, 1966, pages 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" can be undesirable 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 agent should be reasonably fast and should produce images evidencing strong image discrimination with little propensity for 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 principal developing agent. Schestakoff U.S. Pat. No. 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.

Sulfhydroxamic acids are well-known compounds and the preparation is described in the chemical literature. For example, Rodd, *Chemistry of the Carbon Compounds*, (Elsevier Publishing Company, 1954) Volume 3, pages 235–236 describes the preparation of benzene sulfhydroxamic acid.

SUMMARY OF THE INVENTION

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

$$RSO_2NHOH$$

where R is alkyl having one to 12 carbon atoms, aryl having 6 to 12 carbon atoms or heterocyclic having six to 12 carbon atoms.

The activity of this developing agent in many photographic products is unexpected and unobvious since N-methylbenzene sulfhydroxamic acid is not an active silver halide developing agent.

An object of this invention is to provide active developing agents. A further object is to 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 osication of the agents or fogging of the emulsion. A further object is to produce photographic emulsions which may be proceessed 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 compositions which provide desired sensitometric properties and developing action without objectionable stain.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The sulfhydroxamic acids particularly useful in the invention have the general structural formula:

$$RSO_2NHOH$$

wherein R is an alkyl group, including substituted alkyl groups having one 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 cyclopentyl, methylcyclopentyl, cyclohexyl, cyclohexylbromide, cyclohexenyl, and the like; an aryl group including substituted aryl groups, and having six 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 five or six 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 sulfhydroxamic acids being within the skill of the practitioner in the art.

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

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

A significant feature and advantage of the sulfhydroxamic developing agent is its substantially low propensity for staining, hence the developing agent 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 procesing. A second significant feature and advantage is the increase in speed obtained when the sulfhydroxamic acids are employed with pyrazolidone silver halide developing agents. This aspect of the invention is illustrated by Example 3 which follows.

The mole ratio of sulfhydroxamic acid to pyrazolidone developing agent can vary over a wide range. The selection being 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 preferred mole ratio of sulfhydroxamic acid to pyrazolidone DEVELOPING agent is 1:20 to about 20:1. Another preferred ratio is 1:5 to 2:1. A desirable ratio is 1:1 on a molar basis.

Another significant feature and further advantage of the developing agent is its substantial stability when incorporated in a photographic element. It neither causes or induces spontaneous reduction, nor is the developing agent 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. Pat. Nos. 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. No. 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. Pat. Nos. 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 sulfhydroxamic acid can be located in the photosensitive emulsion layer or in contiguous layers of a photographic element and a pyrasolidone 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 a sulfhydroxamic acid 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. Pat. Nos. 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 emulsions, preparations, addenda, processing and systems can be used as disclosed in *Product Licensing Index*, Vol. 92, December, 1971, publication 9232, pages 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; 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, monobaths, acti-

vator 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 art 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. No. 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, Aug. 1950, pages 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. No. 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. No. 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. No. 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 layer 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. e.g, 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. No. 2,698,236 of Land issued Dec. 28, 1954, silica as described in U.S. Pat. No. 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 de-

scribed herein, especially a 3-pyrazolidone silver halide developing agent.

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

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 developer 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 1,000 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 sulfhydroxamic acid either as the developer 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 naphthols described in deMauriac, 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 cid is preferably employed. The behenate, 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 behenater, 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-octadecyloxydiphenyl-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. No. 3,080,254 issued March 5, 1963, and Workman U.S. Pat. No. 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 Various Sulfhydroxamic Acids

The sulfhydroxamic acids employed in our invention are prepared by the following general procedure:

To a stirred slurry of 69 g (1mole) of hydroxylamine hydrochloride in 200 ml of methanol is added slowly a solution of 54 g (1 mole) of sodium methoxide in 300 ml of methanol. The temperature is kept below 15°C by cooling in a ice bath. The sodium chloride is filtered off and washed with a small amount of methanol. To the combined filtrate and washing is slowly added 0.25 mole of the sulfonyl chloride keeping the temperature below 15°C with ice bath cooling. The mixture is stirred overnight at room temperature about 20°C. In the morning the insolubles are filtered off and the filtrate

evaporated under vacuum. The solid residue is extended four times with 250 ml portions of ethyl ether. The combined ether extracts are cncentrated to dryness and the residue recrystallized from water. All of the compounds have InfraRed absorptions for OH 2.9–3.0μ, NH 3.0–3.1μ, and —SO—7.2–7.5μ, 8.4–8.7μ.

The composition and melting point of these compounds are given in Table I, except for benzenesulfhydroxamic acid (R=phenyl) which is purchased from Eastman Organic Chemicals, No. 4450, named as N-hydroxybenzenesulfonamide.

image of low density and contrast.

Table III

Time of Development to Produce a Density of 2.0 in the Presence of 1-Phenyl-3-Pyrazolidone

Compound Number	Time (min.)
1	4.3
2	2.8
3	2.35
4	3.8
5	3.0
6	2.55
7	5.0
8	4.1

TABLE I.—MELTING POINT AND COMPOSITION OF SULFHYDROXAMIC ACID, R—SO_2NHOH

	R	Melting point, ° C.	Percent by weight											
			Calculated						Found					
			C	H	N	S	Br	Cl	C	H	N	S	Br	Cl
1	Phenyl	113 decomposes												
2	p-Methylphenyl	147–51 decomposes*	45.0	4.8	7.5	17.1			44.7	5.0	7.3	17.2		
3	p-Bromophenyl	147–9 decomposes	28.7	2.4	5.5	12.7	31.7		28.3	2.6	5.4	12.4	31.4	
4	p-Chlorophenyl	129.5–32.5 decomposes	34.8	2.9	6.8	15.5		16.9	34.4	3.0	7.1	15.5		17.2
5	3,4-dichlorophenyl	151.5–2	29.8	2.1	5.8	13.2		29.2	29.8	2.4	5.5	13.0		28.9
6	2-thienyl	124–5	26.8	2.8	7.8	35.8			26.8	2.8	8.0	35.4		
7	Methyl	83.5–87.5**	10.9	4.5	12.6	28.9			11.2	4.5	12.2	28.6		
8	p-Methoxyphenyl	132–4	41.4	4.4	6.9	15.7			41.0	4.5	7.0	15.4		
9	p-Xylyl	157–9	47.7	5.5	7.0	15.9			47.6	5.5	7.1	15.6		
10	m-Carboxyl phenyl	185–9 decomposes	38.7	3.2	6.5	14.7			38.5	3.3	6.3	14.5		
11	2,5-dichlorophenyl	200–201 decomposes	29.8	2.1	5.8	13.2			29.5	2.2	5.9	13.4		

*Beilstein XI, 109; m. 148° C.
**Recrystallized from n-butyl alcohol.

EXAMPLE 2

Developing Properties of Various Sulfhydroxamic Acids

Various sulfhydroxamic acids as listed in Table II are employed in a solution containing 0.02 molar concentration of the developing agent, 0.2 molar sodium sulfite and 0.5 molar sodium hydroxide. Fine grain silver chloride film is exposed to a step wedge and developed in each solution for a series of times at 28°C. The resulting densities measured on an Eastman Model 31A Densitometer are plotted, and the time to obtain a density of 2.0 is determined. The various sulfhydroxamic acids are active developers, although differing in degree of activity.

Table II

Time of Development to Produce a Density of 2.0

Compound Number	R Substituent	Time (min.)
1	Phenyl	10.0
2	p-methylphenyl	7.7
3	p-Bromophenyl	5.4
4	p-Chlorophenyl	8.5
5	3,4-Dichlorophenyl	6.1
6	2-Thienyl	6.0
7	Methyl	18.5
8	p-Methoxyphenyl	11.0

—alanine hydroxamic acid and benzohydroxamic acid completely fail to product an image under the conditions of this example.

EXAMPLE 3

Superadditivity with 1-phenyl-3-pyrazolidone

The experimental conditions are the same as in Example 2 except a 0.002 molar concentration of 1-phenyl-3-pyrazolidone is added to each developer. The activity of all developers is increased as shown in Table III. A solution of the pyrazolidone alone produces an

EXAMPLE 4

Stain Propensity

Twenty milligram samples of the developing agents are placed in 10 ml beakers and 1 ml of (a) 4 percent sodium hydroxide, or (b) 4 percent sodium hydroxide plus 6 percent sodium sulfite is added. Sodium sulfite is used as a preservative. The solution is stirred to dissolve the developing agent. After five minutes the solution is absorbed into 1½ × 2-inch piece of chromatographic paper. This is placed in a jar over water for 24 hours at room temperature. The strips are then drifed and the densities read to neutral transmitted light on an Eastman Model 31A sensitometer in comparison with the untreated paper. The density of the untreated paper is substratcted to give the net stain density.

Table IV shows the stain density produced by a variety of agents including hydroquinone and 2,4-diaminophenol and the sulfhydroxamic acids of our invention.

TABLE IV

Staining Propensity

Agent	Net Stain Density (a) Alone	(b) + Sodium Sulfite
Hydroquinone	1.90	0.34
2,4-Diaminophenol	3.82	2.75
1	0.02	0.01
2	0.02	0.01
3	0.03	0.01
4	0.05	0.02
5	0.05	0.02
6	0.03	0.01
7	0.01	0.00
8	0.02	0.01

EXAMPLE 5

Emulsion Incorporation

Each coating composition is prepared according to the following formulation.

Pigskin gelatin, 12% at 49°C	50 ml
Developing agent in 5 ml methanol	0.01 mole
Surfactant (an alkoxy phenolic wetting agent)	1.0 ml
Glutaraldehyde, 2% water solution	0.5 ml
Silver chloride photographic emulsion, at 40°C	5.0 ml

The photographic emulsion is a fine grain silver chloride emulsion containing 124 grams of gelation and one mole of silver in 2.6 kilograms or about 42 mg Ag/ml. Coatings of eight developing agents are made of 0.005-inch wet thickness on baryta-coated paper base and dried in air.

A strip of each coating is exposed through a 0–3.0 step tablet at the 10^{-3} setting of an Edgerton, Germeshausen and Grier Sensitometer, Mark VI. Relative speed in terms of log E is measured at 0.5 density above fog with hydroxylamine sulfate as the standard, as shown in Table V.

Each strip is immersed in an activator solution containing

Sodium hydroxide	10 g
Sodium sulfite	5 g
Sodium sulfate	10 g
Water to	100 ml

for 10 seconds with continuous agitation, then stopped with a 15-second treatment in 4 percent acetic acid solution. Fixation consists of two minutes in sodium thiosulfate fixing solution. Each strip is then washed for 10 minutes at 10°C. All strips are dried in air at room temperature.

The compounds tested and the results obtained are indicated in Table V. Hydroxylamine is included for comparison. It will be noted that all of the sulfhydroxamic acids produce an appreciable degree of development.

EXAMPLE 6

Keeping Properties

Strips of coating prepared as in Example 5 containing hydroxylamine sulfate; benzenesulfhydroxamic acid and p-toluene sulfhydroxamic acid are packaged in unsealed 8 × 10-inch envelopes and incubated for 14 days at 120°F and 35% R.H. The incubated strips are then processed as in Example 5. The coating containing the hydroxylamine sulfate shows a speed loss of 0.20 log E units. That containing the benzenesulfhydroxamic acids shows a gain of 0.04 log E units and that containing the toluene sulfhydroxamic acid 0.14 units. There is no loss in contrast and little change in fog. Similar coatings made with hydroquinone show large losses in speed and contrast. Thus, the developing agents of our invention show incubation advantages over compounds such as hydroquinone and hydroxylamine. D_{max} and D_{min} values are net values above the density of the paper base.

TABLE V

Sensitometric Parameters, Aqueous Activation

	Gamma (Fresh)	Relative Speed (Log E) (Fresh)	D_{max} (Fresh)	D_{min}* (Fresh)
Hydroxylamine sulfate	1.10	0.00	1.46	0.24
Methanesulfhydroxamic acid	1.85	−0.06	1.30	0.26
N-Hydroxybenzene Sulfonamide (Benzenesulfhydroxamic acid)	1.26	+0.02	1.58	0.22
p-Bromobenzenesulfhydroxamic acid	0.84	+0.16	1.42	0.22
p-Toluenesulfhydroxamic acid	1.02	+0.10	1.46	0.22
m-Carboxybenzenesulfhydroxamic acid	0.54	−1.30	0.70	0.12
p-X-ylenesulfhydroxamic acid	0.82	+0.02	1.45	0.28
2-Thiophensulfhydroxamic acid	1.58	+0.22	1.88	0.26

* Density of paper base = 0.13

EXAMPLE 7

Use in Diffusion Transfer Process

The following solution is prapared:

Sodium sulfite	20 grams
Sodium thiosulfate · $5H_2O$	10 grams
4-methyl-1-phenyl-3-pyrazolidone	1.76 grams
Benzenesulfhydroxamic acid 8.65 grams	
Water to	1000 cc
Sodium hydroxide sufficient to produce pH	13.5

A silver chlorobromide emulsion is exposed to a sensitometer as in Example 5 and contacted with a receiver layer which contains Carey Lea silver on a support. The receiver is prebathed in the above formulation for two minutes. The receiver and negative are laminated together for a period of 10 minutes at room temperature. Duplicates are made, one of which receives no further treatment on delamination and the other is washed and dried. A negative of good quality is obtained, while the image in the receiver has high contrast and density. It is free from stain even when not washed following delamination.

EXAMPLE 8

Use in Dry Processing

Compounds 2, 3, 9, 10 and 11 of Example 1, Table I, are incorporated at a concentration of approximately 1 millimole in 8 ml of an emulsion containing 0.4 millimole of silver chloride, 0.5 millimole of a stabilizing agent consisting of chloride and trifluoroacetate salts of 1,8-(3,6-dioxaocetane) bis-isothiurea, 1 millimole of 5-methyl-1-phenyl-3-pyrazolidone and about 10 percent by weight pigskin gelatin. This emulsion is coated on a polyethylene-coated paper photographic support. It is processed by holding in contact for 5 seconds with a mandril heated to 200°C. Images of good density are produced when the sulfhydroxamic acids are added to the emulsion as compared with a very weak image produced in its absence. The images are stable to further exposure to light.

EXAMPLE 9

Photothermographic System

The light-sensitive medium is similar to that described by Morgan in U.S. Pat. No. 3,457,075 and comprises a mixture of silver behenate, behenic acid, a silver bromide sensitizer, and phthalazinone toning agent in a polyvinyl butyral vehicle. A 0.1 molar solution of benzenesulfhydroxamic acid in a mixture of acetone and methanol is placed on the surface of the emulsion. After it has dried the emulsion is exposed to light and then heated to terperatures of 100° and 140°C. Strong images are produced particularly at 140°C. Images are

also produced when this procedure is repeated employing a coating without the phthalazinone toner, but the images are somewhat less dense and less black. In similar experiments p-tolysulfhydroxamic acid, bromophenyl sulfhydroxamic acid, m-carboxysulfhydroxamic acid, 2-thiophene sulfhydroxamic acid and methanesulfhydroxamic acid are all found to produce strong images.

Hydroxylamine sulfate, an agent of the prior art, fails to produce an image when tested under these conditions.

The concentrations of the developer employed in accordance with the invention can vary over wide ranges depending upon the particular photographic system. Typical of the variables which effect the concentration of the developing agents are the location in the photographic element, the developer composition, the desired image, etc. Suitable concentrations are also dependent on processing conditions, addenda present in the photographic element to be processed and/or in the processing compositions. Suitable optimum concentrations can be easily determined by those skilled in the art through routine experimentation. Typically, when a developer described herein is incorporated in a photographic element, the concentration can vary from about 10 to about 400 g of developer per mole of silver present in the photographic element. A MORE PREFERRED range is from about 40 to about 200 g per mole of silver present. When a developing agent as described is employed in a developing composition for processing of a photographic element, the total concentration of developing agents can vary from about 2 to about 100 g/l and preferably from about 5 to about 40 g/l.

As employed in a "dry photographic" element the sulfhydroxamic acids of this invention can be present in an amount of from about 0.1 to about four moles per mole of catalyst and preferably from about 0.5 to about two moles per mole of catalyst.

The particular time required for developing the photographic elements described herein can vary over a wide range such as from about a few seconds up to an hour or more, depending on the photographic element utilized, the desired image, the various addenda employed, etc. The optimum developing time can be obtained by routine experimentation.

Silver precipitating or development nuclei or agents which can be employed in diffusion transfer systems as described can be physical development nuclei or chemical precipitants including: (a) heavy metals in colloidal form and salts of these metals, (b) salts of amines which form silver salts and/or (c) non-diffusion polymeric materials with functional groups capable of combining with the silver amine. Suitable silver precipitating agents and/or nuclei within the above classes include metal sulfides, selenides, polysulfides, polyselenides, thiourea derivatives, stannous halide, silver, gold, platinum, palladium, and mercury, colloidal silver and similar agents disclosed, for example, in U.S. Pat. No. 3,020,155 of Yackel et al. issued Feb. 6, 1962. A wide range of concentrations of the silver precipitating agents and nuclei can be employed. The concentration of silver precipitant or nuclei in the receiving layer or receiving sheet must be at least sufficient to ensure a positive and sufficient removal of undeveloped silver salt from the light-sensitive layer to be processed. Usually, the concentration of developing agent described is about 3 to about 320 milligrams per square foot of the layer containing the precipitants or nuclei.

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

We claim:

1. A photographic processing composition comprising an alkaline development activator and a sulfhydroxamic acid silver halide developing agent.

2. The composition of claim **1** wherein said sulfhydroxamic acid is represented by the structural formula:

$$RSO_2NHOH$$

wherein R is alkyl having one to 12 carbon atoms, aryl having six to 12 carbon atoms or a heterocyclic group having five or six atoms.

3. A photographic processing composition as in claim **1** comprising an aqueous alkaline solution.

4. The composition of claim **2** wherein R is 4-methyl phenyl; 4-bromophenyl; 3,4-dichlorophenyl or 2-thiophene.

5. A photographic processing composition as in claim **1** comprising an auxiliary silver halide developing agent.

6. A photographic composition of claim **1** comprising a silver halide solvent.

7. A photographic processing composition of claim **6** in which said auxiliary agent is a pyrazolidone silver halide developing agent.

8. A photographic composition of claim **7** wherein the mole ratio of the sulfhydroxamic acid to pyrazolidone is in the range of from about 1:5 to about 2:1.

9. A photographic element comprising a support having thereon at least one photographic silver salt layer, and incorporated in said element as a silver salt developing agent, a sulfhydroxamic acid represented by the structural formula:

$$RSO_2NHOH$$

wherein R is alkyl having one to 12 carbon atoms, aryl having six to 12 carbon atoms or a heterocyclic group having five to six atoms.

10. A photographic element of claim **9** which also comprises a pyrazolidone developing agent.

11. A photographic element of claim **9** wherein said silver salt layer is a silver halide emulsion.

12. A photographic element of claim **11** wherein said photographic developing agent is present in said silver halide emulsion.

13. A photographic element as in claim **11** wherein said developing agent is in a layer contiguous to said silver halide layer.

14. A photographic element as in claim **11** wherein said sulfhydroxamic acid is located in said silver halide emulsion layer and a pyrazolidone developing agent is in a layer contiguous to said silver halide layer.

15. In a process of developing an exposed photographic element, said element comprising a support having thereon at least one photographic silver salt layer, said process comprising contacting said exposed element with a photographic developing agent and activating said developing agent, the improvement comprising employing a sulfhydroxamic acid developing agent represented by the structural formula:

RSO_2NHOH

wherein R is alkyl having one to 12 carbon atoms, aryl having six to 12 carbon atoms or a heterocyclic group having five to six atoms.

16. A process as in claim **15** wherein the development process is activated by heating the photographic element.

17. A process as in claim **15** wherein said developing agent is incorporated in said photographic element.

18. In a photographic emulsion comprising at least one photographic silver salt and a developing composition, the improvement wherein the developing composition comprises a sulfhydroxamic acid developing agent.

19. A process of developing an exposed photographic element, said element comprising a support having thereon at least one silver halide emulsion containing a sulfhydroxamic acid developing agent, said process comprising activating development with an activator solution comprising a pyrazolidone developing agent.

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