United States Patent

Haist et al.

[15] **3,649,279**

[45] **Mar. 14, 1972**

[54] PHOTOGRAPHIC COMPOSITIONS WITH A THIOSEMICARBAZONE SOLUBILIZING AGENT

[72] Inventors: **Grant M. Haist; Wilbert J. Humphlett,** both of Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company,** Rochester, N.Y.

[22] Filed: **Jan. 15, 1970**

[21] Appl. No.: **3,174**

[52] **U.S. Cl.** **96/61,** 96/29

[51] **Int. Cl.** **G03c 5/38**

[58] **Field of Search** 96/107, 61, 29

[56] **References Cited**

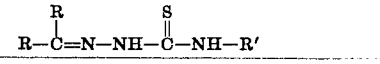
UNITED STATES PATENTS

3,326,689	6/1967	Fix	96/107
2,543,181	2/1951	Land	96/29

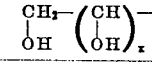
Primary Examiner—Norman G. Torchin
Assistant Examiner—John L. Goodrow
Attorney—W. H. J. Kline, B. D. Wiese and Henry E. Byers

[57] **ABSTRACT**

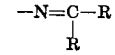
The present invention relates to novel silver halide solubilizing agents having the formula:



wherein R is a substituent selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl, and heterocyclic radicals, and radicals derived from polyhydroxy aldehydes, said radicals having the formula:



wherein x is an integer 1 to 4; wherein R′ is a substituent selected from the group consisting of R and radicals having the formula:



and wherein at least 1 of said R substituents defined above contains a hydroxyl group, i.e. —OH. Also disclosed are photographic compositions, such as monobaths, containing said silver halide solubilizing agents and photographic processes using said composition.

13 Claims, 4 Drawing Figures

FIG. 1

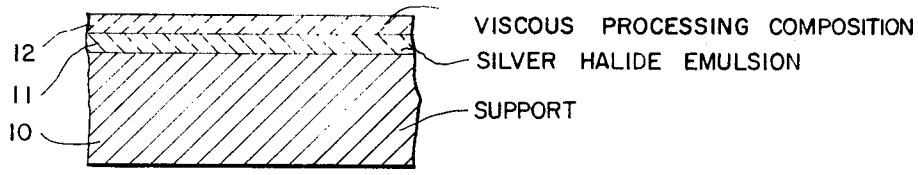


FIG. 2

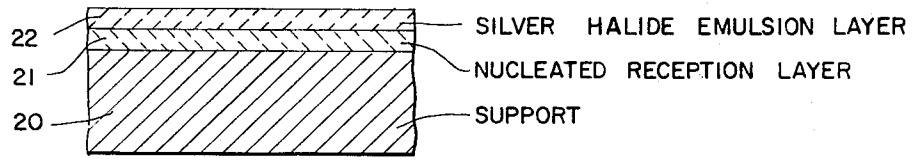


FIG. 3

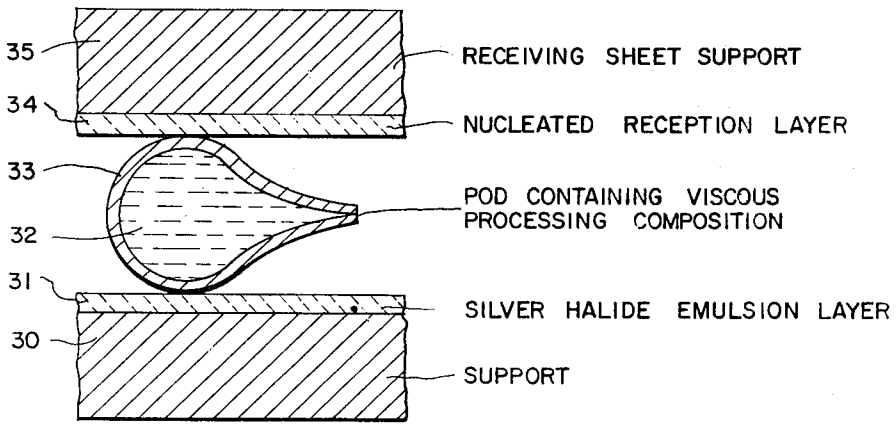
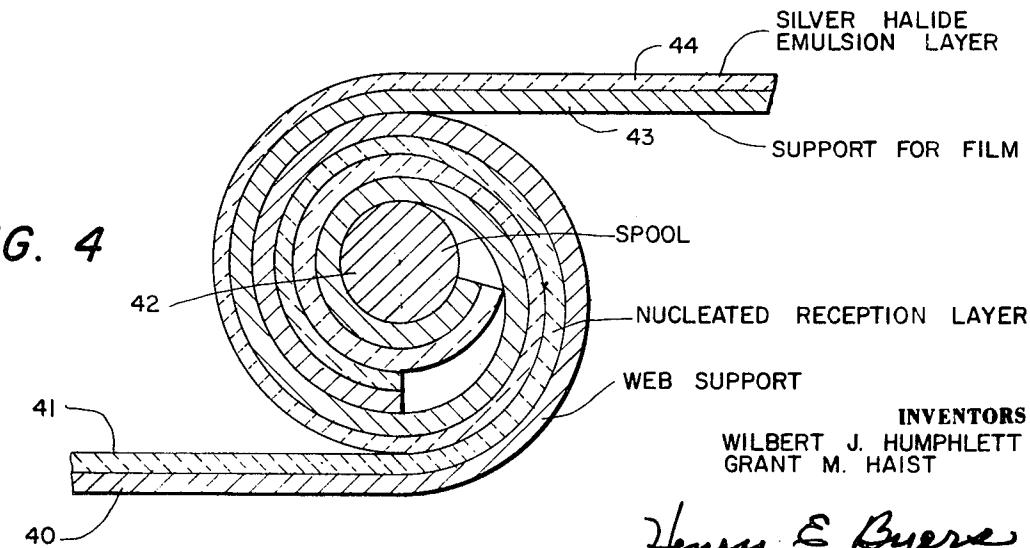


FIG. 4



INVENTORS
WILBERT J. HUMPHLETT
GRANT M. HAIST

BY Henry E Byerve

ATTORNEY

PHOTOGRAPHIC COMPOSITIONS WITH A THIOSEMICARBAZONE SOLUBILIZING AGENT

FIELD OF THE INVENTION

The present invention relates to novel silver halide solubilizing agents and photographic compositions containing said agent.

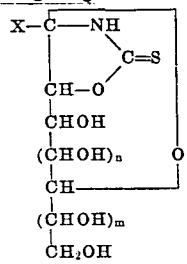
STATE OF THE ART

Developed photographic silver halide emulsion layers are fixed or stabilized by a chemical treatment in order to produce a permanent silver image. If the residual silver halide is left in the developed emulsion layer, it would be converted to silver upon exposure to light and thus obliterate the image. To avoid this, developed photographic silver halide emulsion layers are commonly fixed by using a fixing agent which forms a water-soluble complex which is then washed out of the emulsion layer along with the fixing agent. Such fixing agents as a class are silver halide solubilizing materials.

Silver halide solubilizing materials are also utilized in chemical transfer processes wherein unexposed and undeveloped silver halide is transferred to a receiving sheet or a web, the solubilizing agent facilitating the transfer of such silver halide.

Silver halide solubilizing agents also have utility in so-called "monobaths" wherein a single processing solution can be utilized to both develop and fix a photographic silver halide emulsion layer.

Various examples of silver halide solubilizing agents are known in the art. One example is the thiosugar silver halide solubilizing agents having the general formula:



wherein X is a hydrogen atom or a methanol radical ($-CH_2OH$), n is an integer of 0 to 1 and m is an integer of 0 to 3. These thiosugar silver halide solubilizing agents are disclosed in said U.S. Pat. No. 3,220,838, issued Nov. 30, 1965. It will be noted that the thiosugar solubilizing materials disclosed in said patent are generally utilized in alkaline media. Accordingly, development of a novel silver halide solubilizing agent useful in acidic and neutral aqueous media as well as alkaline media would be a welcome addition to the art.

At this point, it should be observed that the silver halide solubilizing agents of the present invention are not to be confused with the antifading materials noted in U.S. Pat. 3,239,340 issued Mar. 8, 1966, (see column 3). Those antifading materials including acetonethiosemicarbazone and benzaldehydethiosemicarbazone are used to prevent fading of an image under high humidity conditions and then only in combination with conventional fixing agents such as the alkali thiosulfates, alkali thiocyanates, ammonium thiosulfate and ammonium thiocyanate.

It is an object of this invention to provide novel compositions having high silver halide solvent activity in acidic, neutral and alkaline media.

It is another object of this invention to provide novel fixing compositions for developed photographic silver halide emulsion layers.

It is another object of this invention to provide a novel process for fixing developed photographic silver halide emulsion layers.

It is another object of this invention to provide novel monobath compositions.

It is also an object of this invention to provide a photographic chemical transfer process wherein a novel silver halide solvent is utilized.

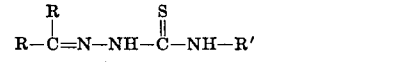
In addition, it is an object of this invention to provide a new viscous processing composition suitable for use in photographic pods of the type utilized with rapid incamera processing films and the like.

Similarly, it is an object of this invention to provide a novel viscous processing composition suitable for use with photographic webs of the type utilized with rapid processing of motion picture film and the like.

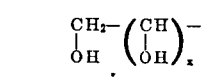
These and other objects of the invention will become apparent from the following discussion:

SUMMARY OF THE INVENTION

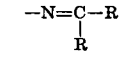
The above and other objects of the invention are accomplished with compositions containing silver halide solubilizing materials having the general formula:



wherein R is a substituent selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl and heterocyclic radicals, and radicals derived from polyhydroxy aldehydes, said radicals having the formula:



where x is an integer of 1 to 4; wherein R′ is a substituent selected from the group consisting of R and radicals having the formula:



and wherein at least 1 of said R substituents defined hereinabove contains a hydroxyl radical, i.e., —OH.

In one aspect of the invention there is provided a photographic chemical transfer method for processing an image-exposed silver halide emulsion layer which comprises developing said silver halide to produce a negative silver image, treating the resulting developed silver halide emulsion layer with an aqueous composition, transferring unexposed and undeveloped silver halide to a reception layer containing a silver halide precipitant, and reducing the said transferred silver halide to silver, said aqueous composition containing at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula shown above.

In another aspect of the invention there is provided a process for solubilizing unexposed and undeveloped silver halide on a photographic element which comprises treating said silver halide with an aqueous composition comprising at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula shown above.

In another aspect of the invention there is provided an aqueous composition containing a silver halide developing agent and at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula shown above.

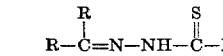
In another aspect of the invention there is provided an aqueous photographic monobath composition being suitable for both developing and fixing photographic silver halide emulsions and comprising a photographic silver halide developing agent and at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula shown above.

In another aspect of the invention there is provided an aqueous viscous photographic monobath composition being suitable for both developing and fixing photographic silver halide emulsions comprising a photographic silver halide developing agent, a viscosity-increasing material and at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula shown above.

These and other aspects of the invention are described in the following discussion:

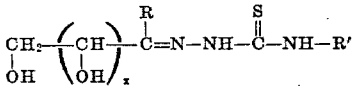
PREFERRED EMBODIMENTS

The subject silver halide solubilizing agent can be represented by the formula:



wherein R and R′ are the same as designated hereinabove.

The alkyl radicals from which the R substituent may be selected generally have one to 10 carbon atoms and can include such non-interfering substituents as alkyl, aryl, sulfonyl, carboxyl, amino, and the like. The aryl radicals from which the R substituents may be selected are of the phenyl or naphthyl series and can include various non-interfering substituents such as alkyl, sulfonyl, carboxyl, amino, and the like. Various heterocyclic radicals contemplated within the scope of this invention are preferably rings having five to six atoms such as morpholino, oxapentamethylene, pyridyl, thiazolyl, and the like. An especially preferred substituent which may be bonded to the various alkyl, aryl, or heterocyclic radicals is the hydroxyl radical (—OH). The hydroxyl radical is preferred as it generally tends to enhance the water solubility of the solubilizing agents. A particularly useful class of solubilizing agents according to the present invention are water-soluble compounds prepared by reacting polyhydroxy aldehydes such as mannose, glucose, galactose, glyceraldehyde and the like with thiosemicarbazide, and which can be represented by the formula:



wherein x is an integer of 1 to 4 and R is hydrogen and R′ is as defined hereinabove.

As will be noted from the above structural formula representing the solubilizing agents of the present invention, said solubilizing agents generally comprise a particular class of thiosemicarbazones and thiocarbohydrazones. Synthesis of these thiosemicarbazones and thiocarbohydrazones can be prepared by reaction techniques and methods well known to those skilled in the art. For example, the thiosemicarbazone solubilizing agents of the present invention can be prepared by reacting a thiosemicarbazide with an aldehyde or a ketone in accordance with usual practice. Reference is made to Berichte 35, 2049, (1902) and Organic Reagents for Organic Analysis, Hopkins and Williams Research Laboratory, Chem. Pub. Co., Inc., New York 94 (1946), for typical methods for preparing such thiosemicarbazones.

Typical suitable solubilizing agents that can be utilized in the present invention include:

L-arabinose thiosemicarbazone
bis(D-glucose) thiocarbohydrazone
dihydroxyactetone thiosemicarbazone
D-glucose thiosemicarbazone
levulinic acid thiosemicarbazone
morpholino-2-propane thiosemicarbazone

and the like.

D,L-glyceraldehyde thiosemicarbazone
D-mannose thiosemicarbazone
D-galactose thiosemicarbazone
morpholino-2-propanone thiosemicarbazone
o-phthaldehyde monoacid thiosemicarbazone
glyoxal bis(thiosemicarbazone)
benzaldehyde (4-phenyl-3-thio)-semicarbazone
o-tolylaldehyde thiosemicarbazone
D-xylose thiosemicarbazone
L-arabinose thiosemicarbazone
propionaldehyde thiosemicarbazone
p-dimethylaminobenzaldehyde thiosemicarbazone
β-morpholinoethylthio-2-propanone thiosemicarbazone
diethylamino-2-propanone thiosemicarbazone
pyridyl-2-aldehyde(4-phenyl-3-thio) semicarbazone
benzaldehyde (4-ethyl-3-thio) semicarbazone
acetone thiosemicarbazone
benzaldehyde thiosemicarbazone
nitrobenzaldehyde thiosemicarbazone
oxapentamethylene-2-propanone thiosemicarbazone
thiazolyl-2-propanone thiosemicarbazone

and the like.

Also, carbohydrazones which can be used include:

D-galactose thiocarbohydrazone
D-mannose thiocarbohydrazone
L-rhamnose thiocarbohydrazone

Double-ended thiocarbohydrazones which may be used include:

bis xylose thiocarbohydrazone

The subject silver halide solubilizing agents are typically utilized in aqueous compositions containing at least about 3 grams of solubilizing agent per liter of composition. However, the amount of such silver halide solubilizing agent utilized can be widely varied, the amount used being readily ascertainable by one skilled in the art for the particular photographic application. Generally, however, the amount of solubilizing agent utilized would vary between about 3 grams and 200 grams per liter of processing composition. When the subject solubilizing agents are utilized in baths for clearing or fixing developed photographic film, at least 5 or 10 to 200 grams of solubilizing agent per liter of processing solution are more generally utilized to obtain fixing within a practical time interval. Lower concentrations, down to about 3 grams of the subject solubilizing agent per liter, are more generally utilized as the silver halide solvent in chemical transfer processing.

As indicated earlier, a particular advantage in the solubilizing agent of the present invention is the fact that these solubilizing agents exhibit fixing or clearing activity in acidic and neutral aqueous media as well as alkaline solution. Generally, the subject solubilizing agents may be utilized in aqueous solutions having a pH less than about 12.0. Although the pH of processing compositions may be varied to a pH higher than about 12.0, it is generally not preferred to do so because the very high pH of such aqueous compositions may tend to fog the silver halide emulsion. Various acidic materials and alkaline materials may be utilized to acquire the desired acidity or alkalinity. Acidic materials such as acetic acid, hydrochloric acid, and the like may be used to achieve the desired acidity. Alkali metal carbonates and hydroxides and amines can be utilized to acquire the desired alkalinity.

Monobaths which can be utilized to both develop and fix an exposed photographic silver halide emulsion are well known in the art. Such monobaths contain both a photographic developing agent suitable for developing or reducing latent silver halide images to silver and a silver halide solubilizing or fixing agent such as ammonium thiocyanate, sodium thiosulfate, and the like. The subject solubilizing agents can be utilized in lieu of the conventional sodium thiosulfate and the like silver halide solubilizing agents in such monobath compositions. Typical silver halide developing agents that can be employed in monobath compositions include such hydroquinonyl compounds as hydroquinone, N-methyl-p-aminophenol-sulfate, chlorohydroquinone, 2,4-diaminophenol and 3,4-diaminophenol hydrochloride; 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, 4-methyl-1-phenyl-3-pyrazolidone and 1-phenyl-4,4-dimethyl-3-pyrazolidone; ene-dioles such as ascorbic acid; catechol; pyrogallol; gallic acid; p-phenylene diamines; and the like, as well as mixtures of such developing agents.

Monobaths of the invention that have high viscosity are particularly useful processing compositions. High viscosity monobath compositions are desirable as they can be readily spread in a uniform layer on the film to be processed. Such compositions desirably have viscosities in excess of about 500 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 20,000 centipoises at this temperature. A wide variety of thickening agents can be added to monobath compositions to impart high viscosities. Such viscosity-imparting materials are film-forming materials

that retain this property and their viscosity in aqueous solution. Suitable viscosity-increasing materials include sodium carboxymethylcellulose, hydroxyethylcellulose, polyvinyl alcohol, sodium salts of polymethacrylic acid and polyacrylic acid, and the like.

The subject thiosugars have particular utility as silver halide solvents in photographic chemical transfer processes. Such transfer processes are well known in the art. Rott in U.S. Pat. No. 2,352,014 described such a transfer process for preparing reversal images. In the Rott process an exposed photographic silver halide emulsion is impregnated with a developer and pressed in contact with a receiving sheet in the presence of a silver halide solvent and a fogging agent. The undeveloped silver halide in the emulsion layer is transferred by means of the silver halide solvent to the receiving sheet, this transferred silver halide developing to silver to form a positive image on the receiving sheet. Other investigators in this field, such as Land, suggested the use of various specific fogging agents or nuclei that could be used in the reception layer to facilitate the formation of a silver image therein and the use of viscous processing materials to facilitate the utilization of processing materials in pods positioned between the light-sensitive negative layer and the reception layer. Reference is made to such Land patents as U.S. Pat. Nos. 2,543,181, 2,584,029 and 2,698,236 for suitable photographic silver halide transfer processes in which the present silver halide solvents can be effectively utilized.

A wide variety of nuclei or silver halide precipitating agents can be utilized in the reception layers used in silver halide solvent transfer processes. Such nuclei are incorporated into conventional photographic organic hydrophilic colloid layers and include such physical nuclei or chemical precipitants as:

a. heavy metals, especially in colloidal form and salts of these metals,
b. salts, the anions of which form silver salts less soluble than the silver halide of the photographic emulsion to be processed, and
c. nondiffusing polymeric materials; with functional groups capable of combining with and in solubilizing silver ions.

Typical useful silver precipitating agents include sulfides, selenides, polysulfides, polyselenides, thiourea and its derivatives, mercaptans, stannous halides, silver, gold, platinum, palladium, mercury, colloidal silver, aminoguanidine sulfate, aminoguanidine carbonate, arsenous oxide, sodium stannite, substituted hydrazines, zanthates, and the like. Polyvinyl mercaptoacetate is an example of a suitable nondiffusing polymeric silver precipitant. Heavy metal sulfides such as lead, silver, zinc, aluminum, cadmium and bismuth sulfides are useful, particularly the sulfides of lead and zinc alone or in an admixture, or complex salts of these with thioacetamide, dithio-oxamide or dithio-biuret. The heavy metals and the novel metals particularly in colloidal form are especially effective. Other silver precipitating agents will occur to those skilled in the present art.

Such silver precipitating or nucleating agents can be utilized in reception layers that are separate elements from the light-sensitive silver halide negative element being processed, or they can be utilized as reception layers integral with the light-sensitive negative element. When the reception layer is utilized as a separate element, the reception layer is typically in the form of a web imbibed with processing material of the type suitable for processing long units of film such as motion picture film, or in the form of a support for receiving positive images of the "snapshot" type that are processed in accordance with the Land patents referred to above. Belgian Pat. No. 472,243 and Tregillus et al., U.S. Pat. Ser. No. 835,473 filed Aug. 24, 1959 describe typical solvent transfer processes utilizing webs as a silver halide reception means. When the reception layer is integral with the light-sensitive negative element, such reception layer is generally a sublayer over which is coated the silver halide in a vehicle that is readily removable during processing such as a hydrophilic colloid soluble in aqueous alkali like cellulose ether phthalate.

FIGS. 1 to 4 illustrate fragmentary views in sectional elevation of typical light-sensitive elements that can be processed in accordance with the invention as well as typical processing methods of the invention utilizing the present silver halide solubilizing agents.

FIG. 1 illustrates a typical light-sensitive element comprising support **10** having coated thereon silver halide emulsion layer **11**. The above-described monobath compositions containing both a developing agent and a solubilizing agent of the invention thickened to a high viscosity with a thickening material can be spread on the surface of layer **11** as illustrated by viscous composition **12** in the drawings. After the processing period, the viscous processing composition thereafter is typically removed from the silver halide emulsion layer by wiping, squeegeeing or by washing.

FIG. 2 of the drawings illustrates a typical light-sensitive element having an integral nucleated reception layer that can be utilized to prepare positive images without the necessity of a separate image receiving sheet. On support **20** is coated nucleated reception layer **21** which is typically an organic hydrophilic colloid material such as hardened gelatin containing any of the nucleating agents described above. Over layer **21** is coated silver halide emulsion layer **22** comprising silver halide dispersed in a substrate that can be readily removed during or after processing. In the processing of a light-sensitive element of the type illustrated in FIG. **2**, a latent image is formed in silver halide emulsion layer **22** on exposure. The resulting exposed element can thereafter be treated with a monobath composition of the type described above either by immersing the element in a solution of the monobath or by coating the surface of the element with a viscous monobath processing composition, such monobaths containing the present silver halide solubilizing agents. During processing, a silver negative image is developed in silver halide emulsion layer **22** and unexposed and undeveloped silver halide in this emulsion layer is transferred to nucleated reception layer **21**. In the nucleated reception layer, the transferred silver halide develops to form a positive silver image. Silver halide emulsion layer **22** containing the negative silver image is removed either during the course of the processing by the aqueous processing composition or by subsequently washing off.

FIG. **3** of the drawing illustrates a typical light-sensitive negative element and a sheet for receiving images transferred from the negative element. Also included in FIG. **3** is a pod containing a viscous processing composition positioned between the light-sensitive negative element and the receiving sheet. In FIG. **3** on support **30** is coated silver halide emulsion layer **31** which serves as the light-sensitive negative element or film material. The receiving sheet comprises support **35** having coated thereon nucleated reception layer **34**. Typical nucleating agents are described in detail hereinabove. Positioned between the receiving sheet and the light-sensitive negative element is pod **31** containing viscous processing composition **32**. Viscous processing composition **32** can be any of the viscous monobaths described above. After exposure of the light-sensitive negative element, a latent image is formed in layer **31**. Processing of this light-sensitive element is effected by drawing the sandwiched layers illustrated in FIG. **3** through rollers to rupture pod **33** and spread a uniform layer of viscous processing composition **32** between silver halide emulsion layer **31** and nucleated reception layer **34**. The latent negative image is developed to silver in layer **31** and remaining unexposed and undeveloped silver halide in layer **31** is transferred to nucleated reception layer **34** wherein it is developed to form a positive silver image. On separation of the receiving sheet from the light-sensitive negative element, a positive silver image remains on the receiving sheet. Such a chemical transfer process has particular utility for rapid incamera processing applications.

FIG. **4** of the drawings illustrates a typical processing web spooled or sandwiched with a photographic film to be processed. The processing web comprises web support **40** having coating thereon nucleated reception layer **41**. The

nucleated reception layer comprises an organic hydrophilic substrate having therein development nuclei of the type described above. The photographic film to be processed comprises support **43** having coated thereon silver halide emulsion layer **44**. The web and the photographic film are sandwiched together so that nucleated reception layer **41** of the web is in intimate contact with silver halide emulsion layer **44** of the film on spool **42**. Prior to spooling together the web and the film to be processed, a diffusion transfer processing composition including a solubilizing agent of the invention as a silver halide solvent is imbibed onto the web. The web and the film are left in the sandwiched or wound form on spool **42** until the processing of the silver halide emulsion layer is complete. Thereafter, the film and the web are unwound resulting in a fully processed negative film. In the processing of the film with the web containing a diffusion transfer composition, a negative silver image is formed in silver halide emulsion layer **44** corresponding to regions of exposure, and unexposed and undeveloped silver halide in this layer is transferred to nucleated reception layer **42** and developed to silver. Such web processing techniques have particular utility for processing strips of film such as microfilm and motion picture film up to **100** feet or more in length.

We have found that the subject silver halide solubilizing agents have many superior properties over currently used agents for this purpose. In general, in addition to the advantages noted hereinbefore, the subject agents do not have the strong characteristic odors which characterize many of the conventional sulfur-containing fixing agents, such as thioglycerol, mercaptoacetic acid, diethylaminoethanethiol and others. The present fixing agents produce silver images having colder image tones than conventional fixing agents. Further, emulsions fixed with the present thiosugars exhibit improved detail in shadow areas and desirable light edge effects.

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

EXAMPLE 1

Each of the following thiosemicarbazones are dissolved in the media noted in Table 1 below. A strip of Fine Grain Positive Film (a bromoiodide film of 350 mg. Ag/ft.^{2}) is attached to the arm of a mechanical agitator which completes **2** up-and-down cycles per second, each of the four strokes being one-half inch in length. The fixing activity of these various thiosemicarbazone solubilizing agents is measured as the time it takes the film to clear. Clearing time is measured visually and this time is recorded in Table 1 shown below.

TABLE 1

	Film-clearing time (seconds) 75° F.		
Name of Compound	5% Sodium Acetate 5% Acetic Acid	Water	5% Sodium Carbonate
L-arabinose thiosemicarbazone	95	95	75
bis(D-glucose)thiocarbohydrazone	270	270	—
2-carboxybenzaldehyde thiosemicarbazone	insoluble	insoluble	225
dihydroxyacetone thiosemicarbazone	46	55	40
D-glucose thiosemicarbazone	155	105	90
levulinic acid thiosemicarbazone	partially cleared	partially	93
morpholino-2-propane thiosemicarbazone	140	—	—

Table 1 above shows that the particular examples of various solubilizing agents of the present invention are capable of fixing a silver halide film in acid, water, or alkaline solution. Accordingly the solubilizing agents of this invention are suitable for photographic solutions of all types as illustrated by the wide pH range of the various fixing agents shown in Table 1. The pH range covered by the various examples of Table 1 extends from about 4.0 to about 11.5.

EXAMPLE 2

The following monobath formulation is made with L-arabinose thiosemicarbazone:

distilled water	50 ml.
4-methyl-1-phenyl-3-pyrazolidone	0.2 g.
sodium sulfite, desiccated	3.0 g.
sodium isoascorbate	3.0 g.
hydroquinone	1.0 g.
L-arabinose thiosemicarbazone	4.5 g.
sodium carbonate	5.5 g.
water to make	100 ml.

The above formulation is heated to 120° F. to dissolve the above materials. The pH of the above formulation is about 10.0. Next, a photographic film of the type described in Example 1 above is exposed to a photographic step tablet and processed for 3 minutes at 75° F. in the above illustrated monobath formulation. A black silver image is formed and the silver halide is fixed from the unexposed areas. The developed silver image has a minimum density of 0.04, a maximum density of 1.32, and a gamma of 1.58.

EXAMPLE 3

The following control diffusion transfer solution is formulated:

monomethyl-para-aminophenol sulfate	1.5 g.
hydroquinone	2.5 g.
sodium sulfite, desiccated	10.0 g.
sodium carbonate monohydrate	40.0 g.
water to make	1.0 l.

The above diffusion transfer solution exhibits a pH of about 10.3. A strip of a photographic film as described in Example 1 above is exposed, then immersed in the above shown diffusion transfer solution for 30 seconds at 75° F. The film emulsion is then pressed in contact with a nucleated receiver containing zinc sulfide nuclei in a gelatin matrix for 60 seconds before stripping apart. The result is only a very faint, light tan positive image.

Now one gram of a number of various silver halide solubilizing agents of the present invention are added to 100 ml. portions of the above illustrated transfer solution. The above-described processing and transfer procedures are repeated on four different strips of film, each strip of film identical to the film described in Example 1 above. The following results are obtained as shown below in Table 2.

TABLE 2

Solubilizing Agent	Effect of solubilizing agent on film-positive image
dihydroxyacetone thiosemicarbazone	dense, reddish tinted image
L-arabinose thiosemicarbazone	dense, brown colored image
levulinic acid thiosemicarbazone	dense, brown colored image
glucose thiosemicarbazone	dense, brown colored image

Comparing the results obtained without solubilizing agent with the results illustrated in Table 2 above, it is apparent that

the silver halide solubilizing agent of the present invention produces dense positive transfer images whereas a diffusion transfer solution without the solubilizing agent of the present invention exhibits a light, very poor density positive image.

EXAMPLE 4

A viscous diffusion transfer solution may be made by adding a viscosity imparting material to the solution described above in Example 3. This may be accomplished by making a 1-liter aqueous solution containing the same components listed in Example 3 above and in addition adding 10 grams of L-arabinose thiosemicarbazone solubilizing agent and 10 grams of hydroxyethylcellulose as a viscosity imparting material. The viscosity of the resulting 1-liter composition is about 25 c.p.s. Pods may be prepared for the above processing composition from aluminum foil lined with polyethylene. Ten-milliliter portions of the processing composition may then be heat sealed into the pods. A negative film comprising a high-speed, coarse-grain, negative-type, developing-out gelatino-silver bromoiodide emulsion on a cellulose acetate film support and a receiving sheet comprising a white-colored cellulose acetate film support having coated thereon a gelatin layer containing nickel sulfide nuclei are then readied for use. Processing may be carried out by positioning a pod containing the processing composition between the receiving sheet and the negative film as illustrated in FIG. 3 of the drawings. The resulting sandwich may then be pulled between rollers to rupture the pod and spread a uniform layer of processing solution between the negative film and the receiving sheet. The layers of the sandwich may be left in contact for about 2 minutes at about 75° F. On separation of the receiving sheet and the negative film, a positive silver image is present on the receiving sheet.

EXAMPLE 5

The silver halide solubilizing agents of the invention may also be used in producing direct-positive images without the aid of a separate receiving sheet or element. A light-sensitive photographic film of the type illustrated by FIG. 2 in the drawings is prepared by coating on a transparent cellulose acetate base a sublayer of hardened gelation containing zinc sulfide nuclei. Over the resulting layer is coated a high-speed, coarse-grain, negative-type, developing-out emulsion of silver bromoiodide in a soluble cellulose ether phthalate substrate. The resulting film is exposed in an intensity scale sensitometer and thereafter processed for about 4 minutes at 75° F. in the following processing composition:

sodium sulfite, desiccated	75 g.
potassium bromide	1.0 g.
4-methyl-1-phenyl-3-pyrazolidone	1.0 g.
sodium isoascorbate	3.0 g.
hydroquinone	8.0 g.
L-arabinose thiosemicarbazone	15.0 g.
sodium carbonate	30.0 g.
water to make	1 l.

During the processing of the exposed film, a negative silver image is developed in the silver halide cellulose ether phthalate layer. Unexposed and undeveloped silver halide in this layer is dissolved by the solubilizing agent in the processing composition and is transferred to the hardened gelatin zinc sulfide nuclei-containing underlayer wherein the silver halide is developed or is reduced to silver to form a positive silver image. As the cellulose ether phthalate is soluble in aqueous media, the cellulose ether phthalate containing the negative silver layer is readily washed away leaving a positive silver image.

EXAMPLE 6

The subject thiosugars can also be utilized in viscous monobath processing compositions as silver halide solvents in processes not utilizing silver halide reception elements. The following processing composition was prepared:

methylaminoethanol-sulfur dioxide-addition product (17.8% SO_2)	75.0 g.
4,4-dimethyl-1-phenyl-3-pyrazolidone	2.0 g.
hydroquinone	10.0 g.
L-arabinose thiosemicarbazone	45.0 g.
potassium iodide	0.5 g.
pH	10.5
water to make	1.0 l.
colloidal silver (Carey Lea Silver)	0.2 g.
natrosol (hydroxyethylcellulose)	0.2 g.

The prepared viscous processing composition is used to process a light-sensitive film comprising a high-speed, coarse-grain, negative-type, developing-out, gelatino-silver bromoiodide emulsion on a cellulose acetate film base. The film is exposed in an intensity scale sensitometer and a layer of the viscous processing composition is spread over the emulsion surface of the film as illustrated in FIG. 1 in the drawings. After 10 minutes at 70° F., the processing composition is squeegeed from the film. A fully processed film having a light- and heat-stable negative silver image results. Unexposed silver halide is removed during the processing. The viscosity of the above solution may be varied by the addition of higher amounts of thickening agents. Useful viscosity ranges cover between 1,000 to 200,000 centipoises.

EXAMPLE 7

The subject thiosugar silver halide solubilizing agents can be utilized in monobaths which are imbibed on processing webs used to develop and fix silver halide emulsion layers. A typical suitable processing composition has the following formulation:

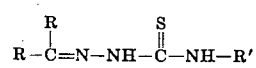
2,2'-iminodiethanol-SO_2 (20% SO_2)	190.0 g.
hydroquinone	11.0 g.
1-phenyl-3-pyrazolidone	1.0 g.
L-arabinose thiosemicarbazone	10 g.
potassium iodide	0.5 g.
water to	1 l.

A process web is prepared by coating on a cellulose acetate support a layer comprising 2 g. of gelatin and 8 mg. of Carey Lea silver per square foot. This web is soaked for about 5 minutes in the monobath processing composition described above at 75° F. prior to winding or coiling in contact with the film to be processed in the manner illustrated in FIG. 4 of the drawings. A high-speed, coarse-grain, negative-type, developing-out, gelatino-silver bromoiodide emulsion coated on a cellulose acetate film support that has been exposed is processed by bringing the silver halide emulsion layer of the film in intimate contact with the nucleated layer of the soaked web and by allowing the resulting rolled sandwich to be maintained for 10 minutes at 75° F. Thereafter, the web and the film are peeled away to leave a fully developed and fixed negative film having a negative silver image in the exposed areas. Similar results can be obtained by utilizing a web prepared from a cellulose acetate film base that is surfaced-hydrolyzed in a sodium hydroxide aqueous ethanol solution for about one hour and thereafter soaked for about 3 minutes in a 0.1 percent gold chloride solution followed by a 3-minute soak in a 0.2 percent solution of N-methyl-p-aminophenolsulfate to form metallic gold nuclei in the hydrolyzed cellulose acetate.

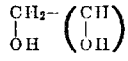
The invention has been described in considerable detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

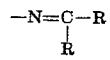
1. An aqueous composition consisting essentially of a silver halide developing agent and at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula:



wherein R is a substituent selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl and heterocyclic radicals, and radicals derived from polyhydroxy aldehydes, said radicals having the formula:

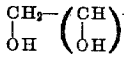


wherein x is an integer 1 to 4; wherein R′ is a substituent selected from the group consisting of R and radicals having the formula:



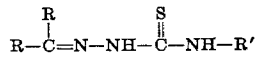
and wherein at least one of said R substituents defined hereinabove contains a hydroxyl radical.

2. An aqueous composition according to claim 1 wherein at least one of said R substituents has the formula:

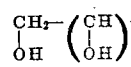


wherein x is an integer 1 to 4.

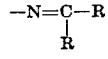
3. An photographic monobath composition being suitable for both developing and fixing photographic silver halide emulsions comprising a photographic silver halide developing agent and at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula:



wherein R is a substituent selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl and heterocyclic radicals, and radicals derived from polyhydroxy aldehydes, said radicals having the formula:

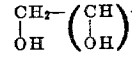


wherein x is an integer 1 to 4; wherein R′ is a substituent selected from the group consisting of R and radicals having the formula:



and wherein at least one of said R substituents defined hereinabove contain a hydroxyl radical.

4. A photographic monobath composition as described in claim 3 wherein at least one of the R substituents of the solubilizing agent has the formula:



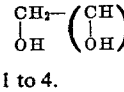
wherein x is an integer 1 to 4.

5. A photographic monobath composition as described in claim 4 wherein the developing agent is a 3-pyrazolidone.

6. A photographic monobath composition according to claim 5 wherein the silver halide solubilizing agent is L-arabinose thiosemicarbazone.

7. A photographic monobath composition according to claim 3 wherein said monobath composition has a viscosity of at least about 500 centipoises at 24° C.

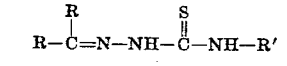
8. A photographic monobath composition according to claim 7 wherein at least one of the R substituents of the solubilizing agent has the formula:



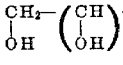
wherein x is an integer 1 to 4.

9. A photographic monobath composition according to claim 7 which has a viscosity of about 1,000 to 200,000 centipoises at 24° C. and wherein the developing agent is a 3-pyrazolidone.

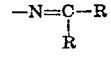
10. A photographic chemical transfer method for processing an image-exposed silver halide emulsion layer which comprises developing said silver halide to produce a negative silver image, treating the resulting developed silver halide emulsion layer with an aqueous composition, transferring unexposed and undeveloped silver halide to a reception layer containing a silver halide precipitant, and reducing the said transferred silver halide to silver, said aqueous composition containing at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula:



wherein R is a substituent selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl and heterocyclic radicals, and radicals derived from polyhydroxy aldehydes, said radicals having the formula:

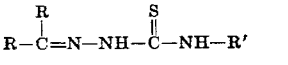


wherein x is an integer 1 to 4; wherein R′ is a substituent selected from the group consisting of R and radicals having the formula:

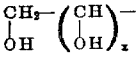


and wherein at least one of said R substituents defined hereinabove contains a hydroxyl radical.

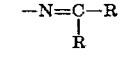
11. The process for solubilizing unexposed and undeveloped silver halide on a photographic element which comprises treating said silver halide with an aqueous composition comprising at least about 3 grams per liter of said composition of a silver halide solubilizing agent having the formula:



wherein R is a substituent selected from the group consisting of hydrogen, substituted and unsubstituted alkyl, aryl and heterocyclic radicals, and radicals derived from polyhydroxy aldehydes, said radicals having the formula:



wherein x is an integer 1 to 4; wherein R′ is a substituent selected from the group consisting of R and radicals having the formula:

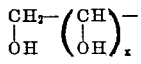


and wherein at least one of said R substituents defined hereinabove contains a hydroxy radical.

12. A process according to claim 11 wherein the silver halide solubilizing agent is a member selected from the group consisting of:

arabinose thiosemicarbazone,
bis(D-glucose)thiosemicarbohydrazone,
2-carboxybenzaldehyde thiosemicarbazone,
dihydroxyacetone thiosemicarbazone,
glucose thiosemicarbazone,
levulinic acid thiosemicarbazone, and
morpholino-2-propane thiosemicarbazone.

13. A process according to claim 11 wherein at least one of the R substituents of the silver halide solubilizing agent has the structural formula:



wherein x is an integer 1 to 4.

* * * * *