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TERTIARY ALIPHATIC PHOSPHINES AS PHOTOGRAPHIC SILVER HALIDE SOLVENTS

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ABSTRACT OF THE DISCLOSURE

Water-soluble tertiary aliphatic phosphines are used as silver halide solvents in photographic processing compositions having a pH in the range of about 4 to 9. In a preferred embodiment, compositions are provided which find particular utility in carrying out diffusion transfer photographic processes at neutrality.

The present invention relates to photography and, more particularly, is concerned with photographic compositions and processes.

In a typical diffusion transfer photographic process, an aqueous composition containing a silver halide developing agent and a silver halide solvent is applied to a photo-exposed silver halide emulsion stratum and a silver-receiving stratum which are maintained in superimposed relation for at least a portion of the processing period. In the emulsion stratum the developing agent reduces the exposed silver halide to silver, and concurrently therewith, the silver halide solvent reacts with unexposed silver halide to form a water-soluble silver complex which is transferred, at least in part, by diffusion to the silver-receiving stratum where it forms a visible image.

Though numerous silver halide solvents are known, those heretofore employed have suffered various drawbacks. Some solvents, such as the sulfites, are effective only with silver chloride and other solvents, such as the alkali metal cyanides, are too poisonous to be practical. In diffusion transfer processes, solvents such as ammonia and certain amines may act as weak solvents while the thiosulfates leave a harmful sulfur residue on the transfer image.

Besides their individual disadvantages, many silver halide solvents are effective in Land diffusion transfer processes only under alkaline conditions so that highly alkaline media having a pH of at least 14 and usually higher are employed. Strongly alkaline processing compositions, due to their instability in air, tend to lose their effectiveness unless they are stored in a closed container and precautions are taken to prevent prolonged exposure of the solution to the atmosphere during packaging and use. Also, in the presence of strong alkali, many undesirable reactions occur or are accelerated, which may lead to deterioration of various components in the photographic system during processing and may result in transfer images which are not particularly stable toward atmospheric poisons (moisture, sulfides, etc.,). Moreover, highly alkaline solutions are frequently objected to for use in any photographic procedure where the materials being developed and fixed are handled manually and may come into contact with the skin. For these and other reasons there has been a continuing effort to find compounds that will be effective silver halide solvents at a pH in the vicinity of 7 so that photographic processing may be carried out in neutral media, and preferably, in plain water containing the essential processing ingredients.

The primary object of the present invention is to provide silver halide solvents that are free from many of the disadvantages associated with those solvents previously used.

A further and particular object of the present invention is to provide silver halide solvents that are highly effective in neutral, slightly acidic and slightly alkaline media.

A still further object of the present invention is to provide compositions and processes, particularly diffusion transfer processes, employing such solvents and to povide reasonably stable transfer images which do not require a separate fixing or stabilizing step.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the compositions and products possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

In copending application of Stanley M. Bloom, Ser. No. 699,300, filed Jan. 22, 1968, organic derivatives of the trihydrides of group VA elements having an atomic number greater than 7 and less than 83 are disclosed and claimed as silver halide solvents for use in photographic processing compositions. As discussed in the application, such compounds are effective with the different silver halides and mixtures thereof commonly used in photosensitive emulsions; may be used in either aqueous or organic solution to form soluble, diffusible silver complexes; are effective complexing agents under less alkaline conditions than are normally employed; and produce good transfer images. Also, such compounds, especially the aliphatic derivatives of such elements, are oxidized in air to give a pale or colorless residue which is not deleterious to the silver transfer image.

According to the present invention, it has now been found that certain of the broad class of silver halide solvents disclosed in the aforementioned copending application are especially useful in aqueous processing compositions which are neutral in character. More particularly, it has been found that tertiary organic phosphines having a solubility in water of at least about 2% by weight at 20° C. are highly effective silver halide solvents in aqueous media having a pH of 7. These phosphines are also effective solvents in weakly alkaline solution, and may be used under weakly acidic conditions as well.

Photographic processing under neutral conditions in accordance with the present invention affords many distinct and important advantages. Certain undesirable reactions are retarded or substantially eliminated, such as, degradative oxidation reactions, e.g., decomposition of the developing agent. accelerated by strong alkali itself and/or by strong alkali in the presence of oxygen

$$(OH^- + O_2 \rightarrow OOH^-)$$

the formation of carbonate ($OH^- + CO_2 \rightarrow CO_3$) and the alkaline hydrolysis of gelatin or other hydrophilic materials used in fabricating photographic emulsions and substrates. Processing at neutrality also allows much greater latitude in the selection of additives. There are toners, sensitizers and other photographic adjuncts that are not suitable for use in highly alkaline media. Where the developing agent, phosphine silver solvent and other processing ingredients are associated with the emulsion and/or image-receiving layers, processing may be activated simply by imbibing with plain water. Besides the benefits derived from using water to initiate processing, the keeping qualities of film structures containing the processing ingredients are greatly enhanced in comparison to films containing alkali in situ.

Processing according to the present invention also affords an opportunity to study the photographic behavior at neutrality of those additives heretofore employed only

in highly alkaline systems. Moreover, neutral processing compositions need not be stored in an air-tight container and whether store din an open or closed container, exhibit considerably improved storage stability. Because tertiary aliphatic phosphines tend to be "self-fixing" and because of the drastically reduced rate of oxidation of developing agent retained in the print, transfer images may be produced which exhibit excellent wall stability even without stabilizing the print by washing. For these same reasons, the steps of stopping and fixing used in conventional photographic processing may be eliminated, if desired, and if the stopping and fixing baths are used, the build-up of alkali residue which alters their chemical composition and tends to impair their function is obviated.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

Preferred tertiary organic phosphines to be employed in accordance with the present invention are tertiary aliphatic phosphines, i.e., compounds of the formula, PR_3, wherein the R groups, the same or different, represent aliphatic radicals. The aliphatic radicals may be saturated or unsaturated, cyclic or acyclic, and may be substituted or unsubstituted. Typical of the aliphatic radicals useful as the R moieties are alkyl, e.g., methyl, ethyl, propyl, butyl; cycloalkyl, e.g., cyclopentyl, cyclohexyl, cyclopropyl; alkenyl, e.g., vinyl, allyl, propenyl; and cycloalkenyl, e.g., cyclohexenyl, cyclooctenyl, cyclopentyl. The substituents of the substituted aiphatic radicals are preferably solubilizing groups, i.e., groups selected to render the compound soluble in aqueous media having a pH in the vicinity of 7. Typical of such substituents are —SO_3H, —OH, —NH_2 and —COOH. Other functional groups that may be present, if desired, include halo, nitro, cyano, carboalkoxy, mercapto, amido and alkoxy. Ordinarily, the R groups are lower aliphatic radicals containing not more than 6 carbon atoms but may contain a larger number of carbon atoms to adjust the diffusion properties where appropriate solubilizing substituents are present. As indicated above, the tertiary aliphatic phosphines selected should be soluble in water to the extent of at least about 2% by weight at 20° C. to ensure satisfactory silver complex formation in aqueous media having a pH not greater than about 9. Any tertiary aliphatic phosphine having the requisite solubility characteristics may be employed. Compounds found to be especially useful are those in which one or more R groups comprise lower alkyl radicals substituted with solubilizing substituents, preferably acid solubilizing groups, e.g., carboxyl groups, and in which any remaining R groups comprise lower alkyl radicals. Such substituents suitably placed render the structures air stable.

Typical compounds corresponding to the foregoing general formula include:

$CH_3CH_2P(CH_2CH_2COOH)_2$

$P(CH_2CH_2COOH)_3$

$CH_3—P(CH_2CH_2COOH)_2$

$CH_3—P(CH_2CH_2CH_2COOH)_2$

$CH_3—P(CH_2CH_2CH_2OH)_2$

$CH_3CH_2—P(CH_2CH_2OH)_2$

$P(CH_2CH_2OH)_3$

$P(CH_2CH_2SO_3H)_3$

$(CH_3)_2—P—(CH_2CH_2CH_2SO_3H)$

$CH_3—P(CH_2CH_2SO_3H)_2$

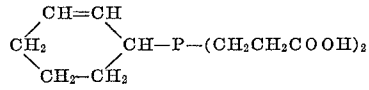
$CH_2=CHCH_2—P—(CH_2CH_2COOH)_2$

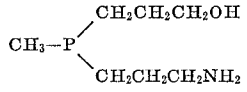
$(CH_3)_2—P—CH_2CH_2COOH$

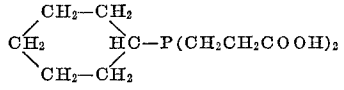
$(CH_3)_2—P—CH_2CH_2CH_2OH$

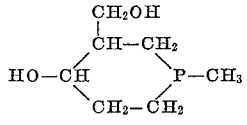
$(CH_3)_2—P—CH_2CH_2CH_2NH_2$

$(CH_3)_2—P—CH_2CH_2CH_2CH_2CH_2NH_2$









In formulating photographic processing compositions utilizing the above-described compounds, a single tertiary aliphatic phosphine may be used or a mixture of two or more such compounds may be employed. The total amount of compound(s) incorporated into the composition may vary widely with the minimum quantity added to the composition being sufficient to give a satisfactory transfer print under the particular processing conditions employed. Ordinarily, the total quantity of tertiary aliphatic phosphine(s) employed in diffusion transfer processing compositions ranges between about 1 and 25% by weight of the processing composition.

To achieve the many benefits of the present invention as enumerated above, the aqueous processing solution should be neutral, weakly alkaline or weakly acidic in nature. For best results, the processing composition should have a pH not exceeding about 9 and generally, should have a pH between about 4 and 9. For obtaining excellent stability during storage and processing, and for obtaining transfer images having superior wall stability, it is desirable that the composition have a pH of about 7. Examples of bases useful in adjusting the pH and capable of imparting the desired alkalinity to the compositions are alkali metal hydroxides, such as sodium, potassium and lithium hydroxides, and amines, such as diethylamine, triethylamine, triethanolamine and allylamine. Examples of acids useful in adjusting the pH and capable of imparting the desired acidity include inorganic acids, such as hydrochloric and nitric acids and organic acids, such as critic and acetic acids. If desired, a suitable buffer system may be employed to maintain the pH of the composition within a predetermined range. Often it is desirable to use the particular phosphine as its own buffer, i.e., the final pH of the resulting photographic processing fluid is then determined by the phosphine itself.

A composition embodying the present invention is broadly useful in a variety of photographic processes of the type in which silver complexes soluble in aqueous media are formed from the unreduced silver halide of a photoexposed and at least partially developed silver halide stratum. The present invention is specifically suitable for use in the production of transfer images wherein the processing composition comprises, in addition to the tertiary aliphatic phosphine complexing agents described above, a suitable silver halide developing agent. The developing agent(s) used may be any of those which are capable of reducing the exposed silver of the latent image at a pH of 9 or below. Typical of such materials are the so-called "inorganic" developing agents, such as chromous, cobaltous, ferrous and titanous ions with appropriate

ligands, such as, ethylenediamine tetraacetic acid, ascorbic acid and oxalic acid and organic developing agents such as aminophenols, e.g., 2,4,6-triaminophenol and 2,4-diaminophenol; alkylaminophenols, e.g., 2,3,5-trimethylaminophenol; 3-pyrazolidinones, e.g., 1-phenyl-3-pyrazolidinone; 3 - aminopyrazolidines, e.g., 1 - p-aminophenyl-3-aminopyrazoline; 4-aminopyrazolones, e.g., 1-phenyl-3-methyl-4-amino-5-pyrazolone; and other organic compounds, e.g., ascorbic acid and dihydroxyfumaric acid. Other developing agents which may be used are the tertiary organic phosphines containing a hydroxyl and/or amino substituted phenyl group as disclosed and claimed in copending application Ser. No. 772,017 of Sheldon A. Buckler and Ronald F. Lambert, filed Oct. 10, 1968. If desired, one or more of the above compounds may be used in combination with other developing agents commonly used in the art.

In one such transfer process, the processing solution is applied in a uniformly thin layer between the superposed surfaces of a photoexposed gelatino silver halide element and an image-receiving element, for example, by advancing the elements between a pair of pressure-applying rollers. The elements are maintained in superposed relation for a predetermined period, preferably for a duration of 15 to 120 seconds, during which exposed silver halide is reduced to silver and unreduced silver halide forms a water-soluble, complex salt which diffuses through the layer of solution to the image-receiving element, there to be reduced to an argental image. At the end of this period, the silver halide element is separated from the image-receiving element. Materials useful in such a transfer process are described in U.S. Pat. No. 2,543,181, issued in the name of Edwin H. Land on February 27, 1951, and in numerous other patents.

The silver halide element may be any of those conventionally used in silver diffusion transfer processes and generally comprises a silver halide emulsion carried on a base, e.g., glass, paper or plastic film. The silver halide may be a silver chloride, iodide, bromide, iodobromide, chlorobromide, etc. The binder for the halide, though usually gelatin, may be a suitable polymer such as polyvinyl alcohol, polyvinyl pyrrolidone and their copolymers.

The image-receiving element preferably includes certain materials, the presence of which, during the transfer process has a desirable effect on the amount ond character of silver precipitated on the image-receiving element. Materials of this type are specifically described in U.S. Pat. Nos. 2,690,237 and 2,698,245, both issued in the name of Edwin H. Land on Dec. 28, 1954.

Separating of the silver halide element from the image-receiving element may be controlled so that the layer of processing composition is removed from the image-receiving element or the layer of processing composition is caused to remain in contact with the image-receiving element, e.g., to provide it with a protective coating. Techniques which enable such results to be accomplished as desired are described in U.S. Pat. No. 2,647,056 issued to Edwin H. Land on July 28, 1953, wherein the processing reagents were selected so that traces remaining after the solidified processing layer had been separated from the silver image or which remained in said layer adhered as a protective coating on the silver image, as indicated above, were colorless or pale, so as not to appreciably affect the appearance of the image and to have little or no tendency to adversely react with the silver image.

The following examples are given to further illustrate the present invention and are not intended to limit the scope thereof.

EXAMPLE 1

A photosensitive element comprising a gelatino silver iodobromide emulsion on film base was exposed to a step wedge and then processed by spreading a layer of processing composition approximately 30 mils thick between the thus-exposed emulsion and a superposed image-receiving element comprising a stratum of regenerated cellulose containing colloidal nickel sulfide as the silver precipitant. The processing composition comprised:

Water: 10 cc.
Hydroxyethyl cellulose: 0.5 g.
2,4,6-triaminophenol·HCl: 0.84 g.
Bis(2-carboxyethyl) methylphosphine·HCl. 0.4 g.
Adjusted to pH 5 with potassium hydroxide.

After an imbibition time of 60 seconds, the image-receiving and photosensitive elements were separated to reveal a silver transfer image of good contrast having a maximum reflection density of 1.0.

EXAMPLE 2

Example 1 was repeated using the same photosensitive and image-receiving elements and the same processing procedure except that the processing composition was adjusted to a pH of 9 with sodium hydroxide. The silver transfer image produced was of good contrast and had a maximum reflection density of 0.6.

EXAMPLE 3

The experiment of Example 1 was repeated using the same materials and procedure except that the processing solution was adjusted to a pH of approximately 4 using lithium hydroxide. Separation of the photosensitive and image-receiving elements revealed a silver transfer image of moderate contrast.

EXAMPLE 4

A gelatino silver iodobromide emulsion on film base was exposed to a step wedge and processed by spreading a layer of processing composition 20 mils thick between the emulsion and a superposed image-receiving element comprising a stratum of regenerated cellulose containing colloidal nickel sulfide as the silver precipitant. The processing composition comprised:

Water: 10 cc.
Hydroxyethyl cellulose: 0.5 g.
2,4,6-triaminophenol·HCl: 0.3 g.
Bis-(2-carboxyethyl) methylphosphine·HCl: 0.5 g.
Adjusted to pH 7 with potassium hydroxide.

After an imbibition time of 60 seconds, the image-receiving and photosensitive elements were separated to reveal a silver transfer image of good contrast having a maximum reflection density of 0.86. When the experiment was repeated using sodium thiosulfate instead of the phosphine as the only silver halide solvent, no silver transfer image was formed.

EXAMPLE 5

The experiment of Example 4 was repeated using an additional 0.2 g. of 2,4,6-triaminophenol hydrochloride in the processing composition which was spread between the photosensitive and image-receiving elements in a layer 30 mils thick. After an imbibition time of 90 seconds, a silver transfer image was obtained which exhibited good contrast and which had a maximum reflection density of 1.20.

EXAMPLE 6

A photosensitive gelatino silver iodobromide emulsion was exposed to a step wedge and superposed on an image-receiving stratum containing silver-precipitating nuclei dispersed in a matrix of colloidal silica coated on a water-impervious base. The following processing composition was spread between the emulsion and image-receiving strata in a layer 30 mils thick:

Water: 10 cc.
Hydroxyethyl cellulose: 0.5 g.
2,4-diaminophenol·HCl: 0.8 g.
Bis-(2-carboxyethyl) methylphosphine·HCl: 0.4 g.
Adjusted to pH 6 with sodium hydroxide.

After an imbibition time of four minutes, the image-receiving stratum was separated from the emulsion to

reveal a silver transfer image of good contrast having a maximum reflection density of 0.72.

In preparing the foregoing compositions, the hydroxyethyl cellulose first was dissolved in water at room temperature. Thereafter, the developing agent and organophosphine were dissolved in the aqueous vehicle, and finally, the hydroxide was dissolved therein. It will be apparent to those skilled in the art that the above processing compositions may be modified by altering the relative proportions of the ingredients and/or by substituting other developing agents, viscosity-imparting reagents and so forth and/or by incorporating preservatives, antifoggants, toners and other adjuncts commonly used in photographic processing fluids.

Since certain changes may be made in the above compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic processing composition comprising an aqueous vehicle having dissolved therein a silver halide developing agent and, as a silver halide solvent, at least one tertiary aliphatic phosphine having a solubility in water of at least about 2% by weight, said composition having a pH between about 4 and 9.

2. A composition as defined in claim **1** wherein said phosphine is a tertiary alkyl phosphine having at least two alkyl substituents containing a water solubilizing group selected from $—SO_3H$, —COOH, —OH and $—NH_2$.

3. A composition as defined in claim **2** wherein said phosphine is bis-(2-carboxyethyl)methylphosphine.

4. A composition as defined in claim **1** wherein the concentration of said phosphine ranges between about 1 and 25% by weight.

5. A photographic method comprising the steps of:

(1) reacting exposed silver halide of a photosensitive silver halide emulsion with a silver halide developing agent in solution in an aqueous vehicle having a pH between about 4 and 9,

(2) reacting unreduced silver halide of said photosensitive emulsion with a tertiary aliphatic phosphine having a solubility in water of at least 2% by weight to form a silver complex that is soluble in said vehicle,

(3) transferring said silver complex to a superposed image-receiving layer, and

(4) reducing said transferred silver complex to provide a silver image.

6. A photographic method according to claim **5** wherein said phosphine is a tertiary alkyl phosphine having at least two alkyl substituents containing a water solubilizing group selected from $—SO_3H$, —COOH, —OH and $—NH_2$.

7. A photographic method according to claim **6** wherein said phosphine is bis-(2-carboxyethyl)methylphosphine.

8. A photographic method according to claim **5** wherein the concentration of said phosphine ranges between about 1 and 25% by weight.

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