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(54) **Photographic processing kit.**

(57) In a photographic processing kit from which an acidic hardening fixer is prepared, a normally solid acid component having pKa of up to 5.0 is present as large size solid particles having a BET specific surface area of 3.00×10^{-3} to 13.0×10^{-3} m^2/g. The acid component in large particle form is effective in preventing a local acute pH drop in the fixer solution during its preparation, thereby preventing sulfide formation in the fixer.

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TECHNICAL FIELD

This invention relates to a photographic processing kit from which an acidic hardening fixer for silver halide black-and-white photosensitive material is prepared.

BACKGROUND OF THE INVENTION

In general, black-and-white photosensitive material is processed, after exposure, through a series of steps including development, fixation and washing using a black-and-white developer, fixer and wash water, respectively. These processing solutions are prepared prior to processing by the user. The developer and fixer kits are usually delivered to the user in the form of liquid concentrates which require only dilution so that the unskillful user can handle with ease. Since such liquid products have leakage and other problems during transportation, recently solid state processing kits, for example, in the form of powder become of interest again.

The fixer for black-and-white photosensitive material generally contains a hardener in the form of a water-soluble aluminum salt. In order to prevent precipitation of $Al(OH)_3$ in the solution, a chelating agent such as tartaric acid and citric acid is added. Also an acidic substance is added in order to adjust the solution to a level of pH 4 to 5 at which maximum film hardening effect is exerted and to impart buffer ability. For either purpose, the addition of acidic substances is essential to the fixer.

If the processing kit from which an acidic hardening fixer is prepared is presented in a solid state like powder, the acidic substances should also be solid or powder. Undesirably, if a fixer is prepared from such a processing kit by dissolving it in water, an abrupt pH drop occurs locally in the solution during the dissolving step whereby the fixing agent or thiosulfate is decomposed into a sulfide. Further, if photosensitive material is processed with such a fixer, there would arise problems such as sulfide staining of the photo-sensitive material during processing and under-fixation due to a lowering of fixing power.

Much sulfide forms particularly with inefficient agitation. For preventing sulfide formation, it will be effective to increase the agitation rate of the dissolving apparatus or to reduce the rate at which the processing kit is admitted to water. Another effective means for preventing sulfide formation is to lower the solution temperature. These approaches are difficult to control and have some limits.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a novel and improved photographic processing kit from which an acidic hardening fixer is prepared without a local abrupt pH drop in the solution and hence without sulfiding.

According to the present invention, there is provided a photographic processing kit from which an acidic hardening fixer containing at least a thiosulfate and a water-soluble aluminum salt is prepared. The kit contains at least one acid component which has a logarithmic value pKa of the inverse of an acid dissociation constant of up to 5.0 as measured at an ion strength of 0.1 mol/liter and 25 ° C and is solid at room temperature. The acid component is present in a solid state and has a specific surface area of 3.00×10^{-3} to 13.0×10^{-3} m^2/g as measured by a BET method. Preferably, the acid component is an organic acid and/or a hardener. Substantially all the components of the kit are present in a solid state.

DETAILED DESCRIPTION OF THE INVENTION

The photographic processing kit according to the present invention is used to prepare an acidic hardening fixer for silver halide black-and-white photosensitive material. The kit contains a plurality of components one of which is at least one acid component which has a pKa of up to 5.0 and is solid at room temperature. The at least one acid component is used in a solid state. It is understood that pKa is a logarithmic value of the inverse of an acid dissociation constant as measured at an ion strength of 0.1 mol/liter and 25 ° C. The room temperature refers to a temperature range between 5 ° C and 30 ° C.

The acid component in a solid state should have a specific surface area of 3.00×10^{-3} to 13.0×10^{-3} m^2/g, preferably 3.00×10^{-3} to 9.0×10^{-3} m^2/g as measured by a BET method. This corresponds to a mean particle size of about 0.5 to 5 mm, preferably about 0.9 to 5 mm. The particle size distribution preferably assumes a nearly mono-dispersed system.

The above-defined range of specific surface area means that the acid component is present as large particles. By comparison, commercially available acid components have a specific surface area of more than 13.0×10^{-3} to 90.0×10^{-3} m^2/g and a mean particle size of about 0.18 to less than 0.5 mm. Large particles are slow to dissolve in water during preparation of the fixer solution. Slow dissolution is effective for suppressing a local abrupt pH drop in the solution and thus preventing the fixing agent or thiosulfate from sulfiding. These benefits of the invention are not available with a specific surface area of more than 13.0×10^{-3} m^2/g because particles are not large enough in size to moderate dissolution. Particles having a specific surface area of less than 3.0×10^{-3} m^2/g are difficult to obtain and the benefits of the invention are no longer enhanced.

It is then unnecessary to achieve sufficient agitation by increasing the agitation rate of the dissolving apparatus or reducing the rate at which the processing kit is admitted to water or to prevent sulfiding by lowering the solution temperature as in the prior art. The present invention allows for ease of preparation of the fixer solution.

In one preferred embodiment wherein the photographic processing kit of the invention takes the form of a vacuum package as will be described later, the specific surface area of the acid component is that prior to vacuum packaging.

The acid component or components used in the kit of the invention serve not only as a chelating agent for preventing precipitation of $Al(OH)_3$ in a fixer containing a water-soluble aluminum salt as a hardener, but also as a pH adjusting/buffering agent for adjusting to an appropriate pH level of 4 to 5 for film hardening and imparting buffer ability. A single acid component serving for both the functions is available while two or more acid components may be used for separate functions. In some cases, a hardener itself is an acid component like ammonium alum.

The present invention may be applied one of such acid components. Where a plurality of acid components are contained in the kit, the present invention is applicable to only one or some or all of them.

Exemplary acid components are organic acids, especially oxy acids used as chelating agents and pH adjusting and buffering agents. Included are tartaric acid, citric acid, gluconic acid, malic acid, and glycolic acid while derivatives of such acids are also acceptable insofar as the requirements of the invention are met. Examples of the hardener include aluminum sulfate and ammonium alum.

To provide a specific surface area in the above-defined range, recrystallization is effective. In particular, an acid component in a commercially available form is dissolved in a suitable solvent, typically water, and allowed to stand for about 8 to 24 hours at room temperature (5 to 20 ° C) for ripening before the precipitate is recovered. When ease of recrystallization procedure is taken into account, the present invention is advantageously applied to such acids as tartaric acid, citric acid, maleic acid and malic acid.

The photographic processing kit containing the specific acid component according to the invention prefers that not only the acid component, but also the remaining components are in a solid state because ease of handling, compactness and transportation advantages are expected.

In one preferred embodiment of the solid state processing kit, those components which should avoid mutual contact are separately packaged. For example, a hardener and an acid component are received in one container while a fixing agent and other components are received in another container.

Also acceptable is a vacuum package wherein components are stacked in multi-layer arrangement such that those components which should avoid mutual contact are separated by an intervening layer (See Japanese Patent Application Nos. 119537/1990, 120612/1990, 138858/1990 and 192259/1990, European Patent Application No. 91 107500.0 filed May 8, 1991, all filed by the same applicant as the present invention, USSN 07/696,884 filed May 8, 1991 by Abe and USSN 07/706,693 filed May 29, 1991 by Hayashi, both assigned to the same assignee as the present invention). Like the separate package, the vacuum package is embodied, for example, by separating a layer containing a hardener and an acid component from another layer containing alkaline components such as a fixing agent and preservative via a neutral substance such as a pH buffer agent (e.g., sodium acetate) to form a multi-layer structure. One exemplary layer structure is a layup of hardener, pH buffer agent, preservative and fixing agent from the bottom to the top. The vacuum packaging offers the advantage of a more compact package.

Where the kit is used within a relatively short time from its preparation so that potential reaction between components is negligible, all the components in powder form may be mixed and received in a single container. Where some components are liquid or desired to store in a liquid state, these components with optional other components in a liquid state may be received in a separate container from a container for solid components.

The acidic hardening fixer to be prepared from the photographic processing kit of the invention is now described. The fixer is an aqueous solution containing a thiosulfate fixing agent at pH 3.8 or higher, preferably pH 4.2 to 7.0, more preferably pH 4.2 to 5.5.

The fixing agents are sodium thiosulfate, ammonium thiosulfate and the like, with the ammonium thiosulfate being preferred in view of fixing speed. The amount of the fixing agent used may be properly selected although it generally ranges from about 0.1 to about 3 mol/liter.

The fixer further contains a water-soluble aluminum salt serving as a hardener. Examples include aluminum chloride, aluminum sulfate, and potassium alum. The amount of aluminum salt added is up to 3.5 g/liter, preferably 3.5 to 2.5 g/liter calculated as Al.

The fixer may contain an aluminum stabilizer such as tartaric acid, citric acid, gluconic acid or derivatives thereof alone or in admixture of two or more. These compounds are preferably contained in an amount of at least 0.005 mol, especially 0.01 to 0.3 mol per liter of the fixer.

If desired, the fixer may further contain a preservative such as sulfites and bisulfites; a pH buffer agent such as acetic acid, boric acid, citric acid, tartaric acid, malic acid, succinic acid, and glycolic acid; a pH adjusting agent such as sulfuric acid; a fixation promoter; an image protecting agent; a chelating agent having an ability to soften hard water; and the compounds described in Japanese Patent Application Kokai (JP-A) No. 78551/1987.

Among liquid compounds, some can be solid members of the solid state kit. For example, if possible, some liquid compounds are converted into powder form. A certain liquid compound may be directly mixed with another solid component if the amount of the liquid compound added is extremely small.

The photographic photosensitive material which can be processed with the acidic hardening fixer resulting from the photographic processing kit of the invention includes black-and-white photosensitive materials. Examples are ordinary picture-taking negative photosensitive materials and black-and-white print paper, photographic materials and printing photosensitive materials for medical image laser printers, medical direct radiography X-ray-sensitive materials, medical indirect radiography X-ray-sensitive materials, CRT image recording photosensitive materials, and industrial X-ray-sensitive materials.

Such photosensitive materials are exposed imagewise, developed with black-and-white developers and then processed with the fixer mentioned above.

The black-and-white developer used herein contains a developing agent, preferably dihydroxybenzenes as typified by hydroquinone. Like the fixer, it is preferred to prepare the black-and-white developer from a solid state processing kit because the solid state kit has the advantages of ease of transportation and compactness.

In such a processing kit, alkaline agents (e.g., KOH and K_2CO_3) used as pH adjusting or buffer agents are preferably used in the form of particles having a larger size than commercially available ones. Such large sized alkaline agents take a longer time to be dissolved, preventing a local pH rise in the black-and-white developer during preparation. This prevents the dihydroxybenzenes such as hydroquinone from being converted into quinones through interaction with alkali to color the black-and-white developer. Large size particles are obtained by recrystallization from water as previously described.

For the processing of black-and-white photosensitive materials, washing water, stabilizer or the like is used. For the detail of these processing solutions including washing water as well as processing conditions, reference is made to JP-A 267559/1986, 93737/1989, 250947/1989, 71260/1990, 103035/1990, and 103037/1990.

EXAMPLE

Example 1

Examples of the present invention are given below by way of illustration and not by way of limitation.

The following fixer components were used. All these components were solid and weighed for addition to 400 ml of water.

$(NH_4)_2S_2O_3$	110 g
Na_2S2O_3	20 g
Na_2SO_3	15 g
Ammonium alum	25 g
Tartaric acid	3 g
Sodium acetate	25 g

The fixer components were separately packaged in two bags by charging a first polyethylene bag with ammonium alum and tartaric acid and a second polyethylene bag with the fixing agent and other components. This set is designated Processing Kit I. The ammonium alum and tartaric acid were used in commercially available form. Their BET specific surface area and mean particle size are reported below as well as pKa (at 25 ° C and an ionic strength of 0.1 mol/liter).

	Specific surface area (m^2/g)	Mean particle size (mm)	pKa
Ammonium alum	$>13.0\times10^{-3}$-90×10^{-3}	0.18-<0.5	1.92
Tartaric acid	$>13.0\times10^{-3}$-40×10^{-3}	0.25-<0.5	4.37

Processing Kit II was obtained by the same procedure as Processing Kit I except that the commercially available tartaric acid was replaced by recrystallized particles of a larger size. Recrystallization was done by dissolving 190 grams of commercially available tartaric acid in 100 ml of water at 50 ° C, allowing the solution to stand for 8 to 24 hours at room temperature, and thereafter recovering the crystals by filtration. The recrystallized particles had a specific surface area of 6.0×10^{-3} to 9.0×10^{-3} m^2/g and a mean particle size of 0.9 to 1.5 mm.

Processing Kit III was obtained by the same procedure as Processing Kit I except that the commercially available ammonium alum was replaced by recrystallized particles of a larger size. Recrystallization was done by dissolving 15.0 grams of commercially available ammonium alum in 100 ml of water at 50 ° C, allowing the solution to stand for 8 to 24 hours at room temperature, and thereafter recovering the crystals by filtration. The recrystallized particles had a specific surface area of 8.5×10^{-3} to 13.0×10^{-3} m^2/g and a mean particle size of 0.5 to 1 mm.

Processing Kit IV was obtained by the same procedure as Processing Kit II except that the commercially available ammonium alum was replaced by the recrystallized particles used in Processing Kit III.

Fixers I to IV were prepared by dissolving Processing Kits I to IV in 400 ml of water, respectively.

Fixers I to IV were visually observed for liquid state. Sulfiding was observed in Fixer I whereas no sulfides were found in Fixers II, III and IV.

Next, a commercially available printing black-and-white photosensitive material (trade name RO-100II manufactured by Fuji Photo-Film Co., Ltd.) after exposure was processed through a series of steps: development (38 ° C/20 sec.) → fixation (38 ° C/10 sec.) → rinse (25 ° C/5 min.), while using a commercially-available black-and-white developer (trade name LD-835 manufactured by Fuji Photo-Film Co., Ltd.), each of Fixers I to IV, and washing water.

The processed photosensitive materials were visually observed for staining. For each of the photosensitive materials, the fixing speed or clearing speed was determined at 25 ° C. The clearing speed was evaluated by measuring a clearing time taken until a transmission density of 0.05 or lower was reached. A clearing time of more than 12 seconds was labeled under-fixation.

Fixer I was found to have stained the photosensitive material at the end of processing and required a clearing time of 13 seconds, indicating under-fixation probably due to a deteriorated processing capacity of the fixer by decomposition of the fixing agent. In contrast, Fixers II to IV caused little or no staining of photosensitive material, especially no staining with Fixer IV. Fixers II, III and IV showed a clearing time of 10.1 sec., 10.1 sec. and 10.0 sec., respectively, giving rise to no problem.

Example 2

Instead of the separately packaged kit as used in Example 1, a vacuum packaged processing kit was prepared by using the same components as in Example 1, successively introducing the respective components in a polyethylene-coated aluminum foil bag so as to form the layer arrangement shown below, and sealing the bag under vacuum. Depending on the particulate form of ammonium alum and tartaric acid, vacuum packages were designated Vacuum Package Kits A, B, C and D in accordance with Processing Kits I, II, III and IV.

Layer arrangement: (1) top, (6) bottom	
(1) $(NH_4)_2S_2O3$	110 g
(2) Na_2S2O_3	20 g
(3) Na_2SO_3	15 g
(4) Sodium acetate	25 g
(5) Tartaric acid	3 g
(6) Ammonium alum	25 g

As in Example 1, fixers were prepared from Vacuum Package Kits A, B, C and D and used in the processing of photosensitive material. Examined were the liquid state of the fixers, staining of the processed photosensitive material, and under-fixation. Equivalent results to Example 1 were obtained depending on the particulate form of ammonium alum and tartaric acid. The vacuum package kits were more compact.

There has been described a photographic processing kit from which an acidic hardening fixer is prepared wherein an acid component is present as a solid having a sufficient specific surface area, typically particles having a sufficiently large size to prevent a local acute pH drop in the fixer solution during its preparation, thereby preventing sulfide formation in the fixer.

Claims

1. A photographic processing kit from which an acidic hardening fixer containing at least a thiosulfate and a water-soluble aluminum salt is prepared, said kit comprising

   at least one acid component which has a logarithmic value pKa of the inverse of an acid dissociation constant of up to 5.0 as measured at an ion strength of 0.1 mol/liter and 25 ° C and is solid at room temperature,

   said at least one acid component being present in a solid state and having a specific surface area of 3.00×10^{-3} to 13.0×10^{-3} m^2/g as measured by a BET method.

2. The kit of claim 1 wherein said acid component is an organic acid, a hardener, or an organic acid and hardener.

3. The kit of claim 2 wherein said acid component is an organic acid selected from the group consisting of tartaric acid, citric acid, gluconic acid, malic acid, maleic acid, glycolic acid and derivatives thereof.

4. The kit of claim 2 wherein said acid component is an aluminum sulfate or ammonium alum hardener.

5. The kit of claim 1 wherein said acid component and substantially all the remaining components are present in a solid state.

6. The kit of claim 5 wherein the components are separately packaged.

7. The kit of claim 5 wherein the components are vacuum packaged in a layer arrangement.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 11 7926

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GRANT HAIST 'modern photographic processing volume 1' 1979 , JOHN WILEY AND SONS (WILEY-INTERSCIENCE) , NEW YORK US * page 575, line 23 - page 576, line 13 * * page 578, line 1 - line 12 * ---	1-4	G03C5/38
A	US-E-RE19354 (F A ELLIOT) * the whole document * ---	1	
A	US-A-2 203 903 (G P HAM) * the whole document * ---	1-6	
A	GB-A-647 409 (KODAK LIMITED) * line 72 - line 95 * ---	1-6	
A	US-A-1 521 840 (S.E SHEPPARD) * page 2, right column, line 90 - line 95 * ---	1-6	
A	EP-A-0 405 238 (AGFA-GEVAERT AKTIENGESELLSCHAFT) * page 1, line 32 - line 35 * -----	1-6	TECHNICAL FIELDS SEARCHED (Int. Cl.5) G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07 DECEMBER 1992	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document