United States Patent Office

3,265,501
Patented August 9, 1966

3,265,501

WATER-SWELLABLE COLLOIDAL MAGNESIUM ALUMINUM SILICATE PHOTOGRAPHIC COMPOSITION

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No Drawing. Filed Dec. 23, 1960, Ser. No. 77,840
14 Claims. (Cl. 96—61)

The present invention relates to viscous photographic processing solutions and to methods of processing photographic material using the same.

It has been of interest for some time to process photographic films and print materials using processing solutions having viscosity such that the processing materials could be placed as a surface layer on an exposed photographic silver halide emulsion coating. By allowing the viscous surface layer to remain on the film for a short period and then removing the layer by washing, photographic materials could be processed readily. In Murray et al. U.S. Patent 2,196,226, issued April 9, 1940, it is proposed to use thickening agents, such as gums, oil starch, gelatin, or glue as thickening agents for developer compositions. As is known in the art, it is often advantageous to use combined developer and fixer solutions, by such use the time necessary for processing a given photographic material can be greatly reduced. In such combined processing solutions, however, it is usually required that silver precipitating agents be incorporated so that fixing of the undeveloped silver halide in the processing photographic material is facilitated. Suitable silver precipitating agents have been described in Rott, U.S. Patent 2,352,014, issued June 20, 1944. It has now been found that surface layer processing solutions can be thickened with a certain water-swellable colloidal metallic silicate to give a viscosity optimum for use in the viscous processing techinque which at the same time obviates the need for silver precipitating agents in compositions comprising fixers, combined developers and fixers, etc. It was very unexpected that the complex colloidal silicate, colloidal magnesium aluminum silicate, could be used both as a thickening agent and a silver precipitating agent without deleteriously affecting the quality of the photographic image. Why the colloidal magnesium aluminum silicate acts in the way that it does in the precipitation of soluble silver halide complexes is not known. It is possible that the magnesium aluminum silicate exchanges magnesium ions for silver ions but if this is occurring, it is very unexpected that deleterious photographic effects do not result. The fact that the water-swellable colloidal silicate of this invention is naturally occurring and usually contains up to 10 percent by weight of foreign minerals renders them even more suspect as unacceptable in a photographic process, since as is known in the art only materials of the highest purity are tolerated in a process which is designed for optimum and uniform quality.

It is therefore an object of the present invention to provide processing solutions having optimum viscosity for use in a viscous processing technique. A further object is to provide viscous processing solutions which do not require the special addition of silver precipitating agents. Another object is to provide new methods for the processing of photographic silver halide emulsion layers utilizing the viscous processing solutions of this invention. Other objects will become apparent from a reading of the specification and appended claims.

These objects are accomplished by incorporating water-swellable colloidal magnesium aluminum silicate into photographic processing solutions to render said processing solutions viscous. By a process of the present

invention, the viscous processing solutions are applied to the surface of an exposed silver halide emulsion layer, allowed to remain for sufficient time to produce the desired photographic result and then removed by convenient means such as washing. A useful range of addition of the water-swellable colloidal magnesium aluminum silicate to processing solutions from about 0.5 percent to about 5.0 percent of the total weight of the composition, with the most useful range being from about 1.0 to about 3.0 percent by weight of the total compositon.

In the present invention any of the conventional processing solutions for photographic processing can be thickened by addition of the water-swellable colloidal magnesium aluminum silicate. Such solutions comprise developers, fixers, combined developers and fixers, combined fixers and hardeners, etc. The present invention, however, is concerned with the incorporation of the water-swellable colloidal metallic silicate as a thickener in viscous monobath and fixing compositions.

In preparing a viscous processing solution, a preferred formulation of the processing composition is selected and prepared as an aqueous solution. The colloidal magnesium aluminum silicate is then dispersed in water with vigorous agitation to form a thickened gel-like composition. The thickening agent is then mixed with the aqueous processing solution to impart to the composition a predetermined viscosity. The thickening agent is of such character as to retain its viscosity—imparting properties in an aqueous alkaline solution so that the processing composition, once its ingredients have been fixed and have attained an equilibrium, remains uniformly viscous for any given temperature for long periods of time. The addition of the thickening agent does not chemically interfere with the processing reactions which are normally encountered. The solutions prepared according to this invention also will tolerate very high salt concentrations without deleterious effects. The thickened processing compositions are easily prepared and have a consistency which is easily applied to the surface of an emulsion layer and readily removed by washing when the particular processing step is completed. The thickening agent is preferably contained in the composition in suitable quantities to impart to the composition a viscosity of at least 100 centipoises at a temperature of 120° F.

In preparing the fixing and combined developing and fixing compositions of this invention, examples of material which can be used in such compositions for the purpose of forming a soluble silver complex with the undeveloped silver halide in the photosensitive layer comprise, for example, alkali metal thiocyanates, alkali metal thiosulfates, ammonium thiocyanate, ammonium thiosulafte, thiloureas, ammonium cyanide, sodium cyanide, etc. When a compound is toxic, such as sodium cyanide, precaution should be taken to prevent an acid condition which would tend to give off poisonous cyanide gas.

Examples of developers useful in the compositions thickened according to this invention alone or in mixture with one another are N-monomethyl-p-aminophenolsulfate; dihydroxybenzenes, e.g., dihydroxydiphenyl; hydroquinone compounds, e.g., chlorohydroquinone, dichlorohydroquinone, bromohydroquinone, and dibromohydroquinone; 1-phenyl-3-pyrazolidone and its derivatives; triaminophenols, including 2,4,6-triaminophenol; catechol; pyrogallol; and ene-diols. Suitable 3-pyrazolidone developing agents include 1-phenyl-4, 4-dimethyl-3-pyrazolidone, 1-p-aminophenyl-4-methyl-4-propyl-3-pyrazolidone, and - 1 - p-chlorophenyl-4-methyl-4-ethyl-3-pyarazolidone. Especially useful to the developing compositions comprise mixtures of monomethyl-p-aminophenolsulfate and hydroquinone; 1-phenyl-3-pyrazolidone and hydroquinone; and 4,4-dimethyl-1-phenyl-3-pyrazolidone and hydroquinone.

The magnesium aluminum silicate for use in the present invention comprises a water-swellable colloidal magnesium aluminum silicate which may contain other admixed materials, such as the minerals which occur in natural admixture with silicates, such as clays, calcium carbonates, calcium sulfates, etc. The water-swellable silicate of this invention in general belongs to the montmorillonite group of minerals and may occur in nature in admixture with various minerals from which it can be separated to a large extent by methods described in U.S. Patent 2,213,643, issued September 3, 1940.

The water-swellable magnesium aluminum silicate should have no greater than 10 percent of its total content made up of foreign minerals, i.e., iron, calcium, titanium, potassium, etc. The hydrous silicate of this invention is readily dispersed in water without soaking, and the dispersions made therewith remains stable for long periods without preservatives. The pH of a dispersion containing from about 4 percent to about 5 percent of hydrous silicate is about pH 9.0.

When in the following examples we refer to Veegum and Biltcote, we are referring to water-swellable colloidal magnesium aluminum silicate.

Veegum and Biltcote have the following chemical composition according to the following publications published by the R. T. Vanderbilt Company, Inc., 230 Park Avenue, New York 17, New York: Veegum, Bulletin No. 44 and Bilt-cote in Paper Coating Colors, Bulletin No. BC 2, July 1, 1962.

	Veegum, percent	Bilt-cote, percent
Silicon Dioxide	61.1	48.7
Magnesium Oxide	13.7	25.5
Aluminum Oxide	9.3	0.6
Titanium Dioxide	0.1	trace
Ferric Oxide	0.9	0.2
Calcium Oxide	2.7	6.3
Sodium Oxide	2.9	1.7
Potassium Oxide	0.3	0.1
Carbon Dioxide	1.8	----------
Lithium Oxide	----------	1.0
Water of Combination	7.2	----------
Loss on Ignition	----------	15.9

Gelatin hardening agents which can be used in the practice of this invention comprise formaldehyde, dialdehydes, potassium alum, β-methyl glutaraldehyde bis-sodium bisulfite, and such agents as described in U.S. Patents 2,080,019, May 11, 1937; 2,725,295, November 29, 1955; 2,725,305, November 29, 1955; and 2,870,013, January 20, 1959.

The following examples are given to further illustrate the invention but there is no intention to be limited thereto.

Example 1

The following example illustrates a manner of fixing a developed silver halide emulsion layer according to the present invention.

An exposed high-speed ortho-chromatic Eastman Kodak Verichrome film was developed and washed in a conventional manner and subsequently fixed with a thickened surface-layer fixer composition prepared as follows:

Thirty grams of Biltcote was dissolved in water with vigorous agitation to make 500 ml. total. Three hundred grams of sodium thiosulfate was then dissolved in 500 ml. of water. The Biltcote dispersion was then added to the aqueous solution of sodium thiosulfate with vigorous agitation until a uniformly thickened dispersion resulted.

The fixing composition was then applied to the surface of the developed silver halide layer at a wet thickness of 0.010 inch and left for 5 minutes at 68° F. After washing, a fixed negative of good quality was obtained.

Example 2

An exposed Kodak Royal Pan sheet film was developed and washed in a conventional manner and subsequently fixed with a thickened surface layer fixer-hardener composition. The composition was prepared as follows:

SOLUTION A

Sodium thiosulfate	grams	240
Sodium sulfite (dessicated)	do	15
28 percent acetic acid	cc	48
Boric acid	grams	7.5
Potassium alum	do	15.0
Water to	ml	500

SOLUTION B

Biltcote	grams	40.0
Water	ml	500

The processing composition was then prepared by mixing the Biltcote dispersion with vigorous agitation with Solution A. The composition obtained was uniformly thickened.

The fixer-hardener composition was then applied to the surface of the developed silver halide layer at a wet thickness of about 0.010 inch and left for 5 minues at 68° F. After washing, a fixed negative of good quality was obtained.

Example 3

A viscous monobath processing solution was prepared as follows:

SOLUTION A

Water to	ml	300
Phenidone	grams	2.2
Hydroquinone	do	20
Sodium sulfite	do	50
Sodium hydroxide	do	15
Sodium thiosulfate	do	125
Water to	ml	500

SOLUTION B

Veegum	grams	20
Water to make	ml	500

The Veegum in water dispersion was agitated vigorously until the colloid was well dispersed.

Solution B was then added to Solution A with vigorous agitation, until a uniformly thickened solution resulted. This solution was then coated onto an exposed Kodak Royal Pan sheet film at a thickness of 0.010 inch and the coating left for 5 minutes at 68° F. Upon washing, the negative was developed and fixed, and the image was of high quality. The thickened layer washed away very easily and was readily disposed of via conventional plumbing systems.

Example 4

A viscous monobath processing solution was prepared as follows:

SOLUTION A

Water to	ml	300
Sodium sulfite	grams	75
Potassium hydroxide	do	7
1-phenyl-4,4-dimethyl-3-pyrazolidone	do	2
Hydroquinone	do	20
Sodium thiosulfate	do	225
Water to make	ml	500

SOLUTION B

Biltcote	grams	10
Water to make	ml	500

The aqueous dispersion of Biltcote was agitated vigorously until the colloid was well dispersed.

Solution B was then added to Solution A with vigorous agitation until a uniformly thickened solution resulted. This thickened solution was then coated on an exposed Kodak Tri-X Reversal film at a wet thickness of 0.015

inch and left in contact for 1 minute at 120° F. After the 1 minute processing, the viscous processing layer was removed with washing to obtain a high quality, developed, and fixed negative image.

A second sheet of Kodak Tri-X Reversal film was processed with a control processing solution prepared according to this example except that gelatin was used as the thickening agent. The thickened monobath according to this control test was applied to the surface of the Kodak Tri-X reversal film and allowed to remain in contact therewith for an optimum period to allow complete development and an opportune time for fixing of the emulsion layer to occur. After washing the viscous monobath from the processed film, only negligible fixing occurred. By carrying out a number of trials, it was found that the monobath prepared according to this example gave the quality of image and completeness of fixation of solubilized silver halide as did thickened fixing agents which had added thereto colloidal silver or some other silver precipitating agent such as those described in U.S. Patent 2,352,014 granted June 20, 1944. Monobaths thickened with colloidal magnesium aluminum silicate obviated the need for the addition of silver precipitating agents without sacrifice of quality.

Example 5

A sheet of exposed Eastman Kodak Super XX Pan film was processed according to Example 3 using a viscous monobath of the following composition:

SOLUTION A

Water	ml	300
Sodium sulfite	grams	50
Sodium hydroxide	do	15
1-phenyl-3-pyrazolidone	do	2
Chlorohydroquinone	do	40
Sodium thiosulfate	do	125
Water to make	ml	500

SOLUTION B

Biltcote	grams	50
Water to make	ml	500

Solution B was agitated vigorously until the colloid was well dispersed. Solution A was then added to Solution B with vigorous agitation to insure uniformity of the dispersion. The processing procedure was according to Example 3 and a high quality developed and fixed negative image resulted.

Example 6

The following monobath gave optimum results in the processing of exposed high-speed Panchromatic negative film.

SOLUTION A

Water	ml	300
Sodium sulfite	grams	50
Sodium hydroxide	do	15
p-Methylaminophenol sulfate	do	2
Hydroquinone	do	20
Sodiumphenylsulfate	do	125
Water to make	ml	500

SOLUTION B

Veegum	grams	30
Water to make	ml	500

Solution B was agitated vigorously until well dispersed and then Solution A was added to it with continued stirring to form a uniform dispersion. The monobath was then applied to the surface of the exposed negative film and allowed to remain in contact for 3 minutes at 68° F. Upon washing, a negative image having completeness of fixation was obtained.

Sodium thiosulfate in the monobaths of the present invention is ordinarily added in the range from about 12.5 to about 30 percent by weight of the total monobath composition. The processing bath need only be applied to the silver halide emulsion layer to be processed at a thickness of about 0.010 to about 0.02 inch to give optimum processing results. The time required to process a layer at this thickness is usually less than 5 minutes at 68° F. Where it is desired to shorten the time of processing, the temperature of reaction or the alkalinity of the processing solution can be raised. By making suitable adjustments, the procedure desired can be formulated. In accordance with the invention the thickened processing solutions are not deleteriously affected by such adjustments.

Improved methods of photographic processing have been obtained using other thickening agents which ordinarily require the separate addition of silver precipitating substances. For example, a monobath processing solution which incorporates a photographic developer and a photographic fixer can be thickened with such thickening agents as carboxy methyl cellulose, hydroxy ethyl cellulose, polyvinyl alcohol, acrylic acid-acrylonitrile copolymer, sulfonated polyvinyltoluene, styrene-maleic acid copolymers, polyvinyl methyl ether-methyl acrylate copolymer, kelgic acid, ethylacrylate-acrylic acid copolymer, and Cab-o-Sil thickener as purchased from Godfrey L. Cabot, Inc. Then in order to facilitate fixing of the undeveloped silver halide and to keep fog formation in the developed film to a minimum, a silver precipitating agent is added to the thickened monobath. Suitable silver precipitating agents comprise colloidal heavy metals, e.g., silver, and metal sulfides, e.g., silver sulfide, zinc sulfide, and nickel sulfide. Other suitable silver precipitating agents are disclosed in U.S. Patent 2,352,014, cited above. In the present invention, however, the special addition of silver precipitating agents is not required in viscous processing solutions, since as shown herein, the colloidal magnesium aluminum silicate acts as both a thickening agent and as a silver precipitating agent.

The advantages of using a viscous surface layer processing solution in the processing of photographic materials are immediately apparent. For example, according to the present invention, photographic films are being processed at all times with a fresh processing solution. As is known in the art, conventional photographic processing solutions undergo changes in composition and therefore changes in activity with use. As more and more film is processed with a given amount of a developer solution, these changes become significant and can ultimately produce unsatisfactorily developed films. Usually, these changes are such that the developer becomes weaker, or less capable of developing sufficient density in the film at a given time of development. To overcome these difficulties, it has been proposed in the art to replenish developer solutions by various means as well as to design developer tanks in such a way as to minimize aerial oxidation, etc. The present invention overcomes these disadvantages by natural means since the silver halide emulsion layer to be processed would contact only fresh processing solutions and the surface layer can be applied sufficiently thin to substantially reduce the overall cost of materials employed in a processing solution. By the use of the thickeners of the present invention, the processing solutions are prepared with a minimum of ingredients and in this manner affords an economy while at the same time producing a uniformity of composition. Another advantage of the present invention is the time saved by combining the developing and fixing steps into a single time-minimized step which requires only a very short processing time to carry out. Further advantages are realized in the ease with which the method of the present invention can be practiced and the fact that elaborate processing equipment is not needed for carrying out the process. It is apparent to those skilled in the art that where a surface layer composition can be employed with satisfactory and optimum results, it is necessary only to have a hopper device for applying the coating with a subsequent washing station for removing the coating after processing. Among the advantages obtained by a surface layer method is the fact that uniformity of result is obtained since the variability of agitation which is normally encountered in the bath-type processing does not occur here.

It will immediately be apparent that the use of colloidal magnesium aluminum silicate as a thickener in viscous processing solutions can be employed not only in the black-and-white variety of processing solution but also in color developing processing solutions. It is also apparent that the colloidal magnesium aluminum silicate of this invention could advantageously be employed in part and also in total in any of the compositions which normally require silver precipitating agents. Particularly where a combination of silver precipitating agents, physical development nuclei, etc., are used with a thickening agent. Clearly, therefore, the present invention relates to the use of colloidal magnesium aluminum silicate in any photographic processing solution.

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

What is claimed is:

1. A method of fixing a photo-exposed and developed silver halide emulsion layer comprising imbibing in said silver halide emulsion layer a viscous photographic silver halide processing solution comprising

(A) a silver halide fixing agent selected from the class consisting of alkali metal thiosulfates, alkali metal thiocyanates, ammonium thiosulfate and ammonium thiocyanate and

(B) a water-swellable, colloidal magnesium aluminum silicate belonging to the montmorillonite group of minerals having at least 90% magnesium aluminum silicate content, in an amount from about 0.5 percent to about 5.0 percent of the total weight of the solution.

2. A viscous photographic silver halide processing solution consisting essentially of:

(A) a silver halide fixing agent selected from the class consisting of alkali metal thiosulfates, alkali metal thiocyanates, ammonium thiosulfate and ammonium thiocyanate,

(B) a water-swellable, colloidal magnesium aluminum silicate in an amount from about 0.5 percent to about 5.0 percent of the total weight of the solution and

(C) water.

3. A viscous photographic silver halide processing solution consisting essentially of

(A) a photographic silver halide developing agent,

(B) a photographic silver halide fixing agent,

(C) a water-swellable, colloidal magnesium aluminum silicate in an amount from about 0.5 percent to about 5.0 percent of the total weight of the solution, and

(D) water.

4. A viscous photographic silver halide processing solution consisting essentially of:

(A) a photographic silver halide fixing agent,

(B) a photographic gelatin hardening agent,

(C) a water-swellable, colloidal magnesium aluminum silicate in the amount from about 0.5 percent to about 5.0 percent of the total weight of the solution, and

(D) water.

5. A viscous photographic silver halide processing solution consisting essentially of:

(A) a mixture of a pyrazolidone developer and hydroquinone,

(B) a photographic silver halide fixing agent,

(C) a water-swellable, colloidal magnesium aluminum silicate in the amount from about 0.5 percent to about 5.0 percent of the total weight of the solution, and

(D) water.

6. A viscous photographic silver halide processing composition consisting essentially of:

(A) sufficient colloidal magnesium aluminum silicate to give a viscosity of at least 100 centipoises at 120° F.,

(B) a photographic developing agent for reducing photoexposed silver halide to silver,

(C) water, and

(D) a water-soluble alkaline material in sufficient amount to render said composition basic.

7. A viscous photographic silver halide processing composition consisting essentially of:

(A) sufficient colloidal magnesium aluminum silicate to give a viscosity of at least 100 centipoises at 120° F.,

(B) a photographic developing agent for reducing photoexposed silver halide to silver,

(C) a photographic silver halide fixing agent,

(D) water, and

(E) a water-soluble alkaline material in sufficient amount to render said composition basic.

8. A method of developing a photoexposed silver halide emulsion layer to a silver image comprising developing said photoexposed silver halide emulsion layer in a viscous photographic silver halide processing composition consisting essentially of:

(A) sufficient colloidal magnesium aluminum silicate to give a viscosity of at least 100 centipoises at 120° F.,

(B) a photographic developing agent for reducing photoexposed silver halide to silver,

(C) water, and

(D) a water-soluble alkaline material in sufficient amount to render said composition basic.

9. A method for developing and fixing a photoexposed silver halide emulsion layer comprising imbibing in said silver halide emulsion layer at least a portion of a viscous photographic silver halide processing composition consisting essentially of:

(A) sufficient colloidal magnesium aluminum silicate to give a viscosity of at least 100 centipoises at 120° F.,

(B) a photographic developing agent for reducing photoexposed silver halide to silver,

(C) a photographic silver halide fixing agent,

(D) water, and

(E) a water-soluble alkaline material in sufficient amount to render said composition basic.

10. A method of fixing a photoexposed and developed silver halide emulsion layer comprising imbibing in said silver halide emulsion layer a viscous photographic silver halide processing solution consisting essentially of:

(A) a silver halide fixing agent selected from the class consisting of alkali metal thiosulfates, alkali metal thiocyanates, ammonium thiosulfate and ammonium thiocyanate,

(B) a water-swellable, colloidal magnesium aluminum silicate in an amount from about 0.5 percent to about 5.0 percent of the total weight of the solution, and

(C) water.

11. A photographic silver halide processing composition for preparing a viscous processing solution consisting essentially of:

(A) a silver halide fixing agent selected from the class consisting of alkali metal thiosulfates, alkali metal thiocyanates, ammonium thiosulfate and ammonium thiocyanate, and

(B) a water-swellable, colloidal magnesium aluminum silicate.

12. A photographic silver halide processing composition for preparing a viscous processing solution consisting essentially of:

(A) a photographic silver halide developing agent,
(B) a photographic silver halide fixing agent, and
(C) a water-swellable, colloidal magnesium aluminum silicate.

13. A photographic silver halide processing composition for preparing a viscous processing solution consisting essentially of:

(A) a photographic silver halide fixing agent,
(B) a photographic gelatin hardening agent, and
(C) a water-swellable, colloidal magnesium aluminum silicate.

14. A photographic silver halide processing composition for preparing a viscous processing solution consisting esesntially of:

(A) a mixture of a pyrazolidone developer and hydroquinone,
(B) a photographic silver halide fixing agent, and
(C) a water-swellable, colloidal magnesium aluminum silicate.

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