United States Patent Office 3,305,364 Patented Feb. 21, 1967

3,305,364

NON-SILVER HALIDE REDUCING SULFONAMIDE BUFFERS FOR PHOTOGRAPHIC DEVELOPING SOLUTIONS

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No Drawing. Filed Sept. 3, 1963, Ser. No. 306,304
13 Claims. (Cl. 96—66.4)

This invention relates to buffers for photographic developers and to photographic developers containing them.

It is well known that the development activity of a particular photographic developer is greatly influenced by the alkalinity of the developer solution. Different developing agents naturally require different levels of pH for optimum development activity. However, the rate of development for many photographic developers depends also on the stability of the pH level of the solution. Therefore, it is evident that to obtain consistent development, the pH of the developing solution should advantageously be kept constant. The pH of the developer also should advantageously be maintained at a high level to obtain a high rate of development. The pH of the developing solution is usually kept constant by the addition of a buffer.

Heretofore, many available buffers in the region of pH 9–13 had certain defects. The phosphate ion, for example, is one of the best available buffers in this pH region but it leads to the precipitation of calcium phosphate, when calcium is present in the water or chemicals used in the developing solution. Many organic buffering agents, such as the guanidines, the phenols and the amino acids, either have too many photographic effects or have been too costly.

It is accordingly an object of our invention to provide novel buffers for photographic developing solutions.

A further object is to provide novel photographic developing solutions containing buffers.

It is another object of our invention to provide photographic developing solutions containing buffers with improved properties.

It is another object of our invention to provide photographic developing solutions containing buffers which will maintain the effective strength of the developing solutions at a high and constant level.

It is another object of our invention to provide relatively inexpensive buffers for photographic developing solutions of high pH.

Other objects will become apparent from a consideration of the following description and examples.

According to our invention, photographic developing solutions are maintained at a high and more constant pH level by the use of a water-soluble, non-silver halide reducing sulfonamide. These compounds can be represented by the following general formula:

(1) $R—SO_2—NH—[(R_1)_{m-1}—NH—SO_2]_{n-1}—R_2$

wherein R represents an alkyl group, such as methyl, ethyl, n-propyl, isobutyl, β-hydroxyethyl, etc. (e.g., an alkyl group containing from 1 to 5 carbon atoms), or an aryl group, such as phenyl, o-, m- and p-tolyl, p-carboxyphenyl, p-sulfophenyl, etc. (e.g., a monocyclic aryl group of the benzene series), R_1 represents an alkylene group, such as methylene, ethylene, etc., *m* and *n* each represents a positive integer of from 1 to 2, and R_2 represents a hydrogen atom, an alkyl group (e.g., an alkyl group as defined above for R) or an aryl group (e.g., an aryl group as defined above for R), when *n* is 1, and R_2 represents an alkyl group (e.g., an alkyl group as defined above for R) or an aryl group (e.g., an aryl group as defined above for R) when *n* is 2.

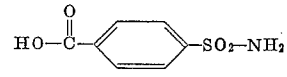
It has also been found in certain instances that a number of the compounds embraced in Formula I above serve to increase the developed density of the photographic element and/or to increase its effective speed, in addition to buffering the pH of the developing solutions. However, because these water-soluble sulfonamides are used in place of the conventional buffers in these developing solutions, they are referred to herein as buffers for photographic developers.

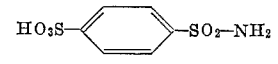
Listed below are a number of compounds coming within the general formula above and which are typical of the buffers of our invention:

(1) $CH_3—SO_2—NH_2$
methanesulfonamide

(2) $CH_3—SO_2—NH—C_2H_5$
N-ethylmethanesulfonamide

(3) $C_2H_5—SO_2—NH—CH_3$
N-methylethanesulfonamide

(4) 
para-carboxybenzenesulfonamide

(5) 
para-sulfo-benzenesulfonamide

(6) $CH_3—SO_2—NH—NH—SO_2—CH_3$
N-(methanesulfonamido) methanesulfonamide

(7) $CH_3—SO_2—NH—C_2H_4—NH—SO_2—CH_3$
1,2-bis(methanesulfonamido)ethane

(8) $CH_3—SO_2—NH—C_2H_4OH$
N-(β-hydroxyethyl)methanesulfonamide

Many of the compounds embraced by Formula I above have been previously described in the prior art. These compounds can be prepared according to the procedure described by Field et al., in J. Am. Chem. Soc., 75, 934–937 (1953). The following specific example illustrates this method.

Example 1

N - ethylmethanesulfonamide, $C_2H_5NHSO_2CH_3$, was prepared from methanesulfonylchloride and ethylamine. Add 100 g. of methanesulfonylchloride to 500 ml. of benzene in a 1-liter round-bottomed flask equipped with dropping funnel, condenser and stirrer. Cool this mixture to 0° C. in an ice bath. Add 78 g. of ethylamine dropwise from the funnel, keeping the temperature below 10° C. After all the ethylamine has been added, allow the reaction mixture to come to room temperature. Filter the mixture to remove the precipitated ethylamine hydrochloride. Remove the benzene by evaporation on a Rinco evaporator. Distill the remaining liquid at a pressure of about 11 mm. using a water pump and a Vigreaux column. Collect the product distilling at 144–149° C. The refractive index of this N-ethyl methanesulfonamide at 25° C. is 1.4900.

Many of the other compounds within the scope of Formula I above can be prepared according to the general procedure set forth above by persons familiar with the art. Thus N-(β-hydroxyethyl)methanesulfonamide can be prepared by substituting β-amino ethanol in place of the ethylamine indicated in Example 1. Similarly, p-carboxybenzenesulfonamide can be prepared by reacting p-cyanobenzenesulfonylchloride with ammonia and hydrolyzing the resultant p-cyanobenzenesulfonamide. The p-cyanobenzenesulfonylchloride can be prepared by the reaction of cyanobenzene with sulfo-chloride.

The water-soluble sulfonamide buffers of the present invention are intended for use with developing solutions

having a pH in the range of about 9.0–13.0. The developing agents used with the buffers of our invention include the well known black and white or color developing agents, such as the phenylenediamines, including the N-alkylphenylenediamines and N-alkyltoluenediamines as well as the p-aminophenols, such as p-aminophenol, N-methyl-p-aminophenol, etc., hydroquinone, the 3-pyrazolidones, e.g., 1-phenyl-3-pyrazolidone, etc. Developing compounds containing an amino group are usually used in the form of the hydrochloride or the sulfate.

The amount of these water-soluble sulfonamides to be added to the developing solution will vary somewhat depending upon the particular developing agent employed and amounts of other ingredients present. In general, we have found that from about .1 to about 200 g. of the buffer per liter of the developing solution is suitable for the purpose of our invention, with a preferred range of from about 1 to about 100 g. of the buffer per liter of the developing solution. The usual addenda can be employed in the developers, such as restrainers (such as potassium bromide), stain preventives, such as alkali metal sulfites, sequestering agents, such as ethylenediamine tetracetic acid, 1,3-diamino-2-propanol tetracetic acid, tetrasodium salt, etc.

The present invention is further illustrated by the following examples. In Example 2, a multilayer color film of the type described in Tong U.S. Patent 2,772,163, was exposed on an intensity scale sensitometer (Kodak Type 1*b*) and developed for 5 minutes at 68° F. in conventional developers containing conventional buffers. Additional test films were similarly exposed and developed in the same conventional developer, but with the conventional buffer replaced by a water-soluble sulfonamide buffer.

Example 2

This example illustrates the use of N-ethylmethanesulfonamide in a color developer of the following composition:

	Conventional Color Developer	Modified Color Developer
Water, liter	1	1
Benzyl alcohol, ml	6	6
Ethylenediamine tetracetic acid, g	4	4
Na_2SO_3, g	5	5
$Na_3PO_412H_2O$, g	40	0
Ethylenediamine, g	2.86	0
N-ethylmethanesulfonamide, g	0	40
KBr, g	0.25	0.25
Citrazinic acid, g	1.4	1.4
Color Developer CD-3 [1], g	11.3	11.3
pH at 75° F	11.57	11.57

[1] 4-amino-N-ethyl-N(beta-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate.

In the modified color developer shown above, the regular buffering agent $Na_3PO_412H_2O$ and the development accelerator ethylenediamine were replaced by N-ethylmethanesulfonamide. The densities of blue D_{max}, indicating the yellow dye yields which are critical for this type film and development, for film developed in these developers were 3.90 for the conventional developer and 3.95 for the modified developer. In addition to the somewhat higher dye yield, the N-ethylmethanesulfonamide buffered developer also avoids what might be a serious dirt problem. The phosphate ion will precipitate insoluble calcium phosphate when hard water is used to make the developer, while the calcium salt of the sulfonamide is soluble.

The buffer capacities of the phosphate and N-ethylmethanesulfonamide are compared in Table I below. The buffer capacity is defined as

$$\frac{dA}{d\text{pH}}$$

where *d*A is a differential addition of an acid to the developer and *d*pH is the change in pH resulting thereby.

TABLE 1

Buffer	G./liter of developer solution	Buffer capacity at pH 11.6
$Na_3PO_412H_2O$	40	0.008
$Na_3PO_412H_2O$	80	0.013
$Na_3PO_412H_2O$	120	0.018
N-ethylmethanesulfonamide	10	0.007
Do	20	0.012
Do	40	0.020

Since phosphate ion is one of the best available buffers in this pH region, Table 1 shows that the sulfonamide is at least equally good.

Example 3

This example compares the use of methanesulfonamide with the regularly used sodium carbonate buffer in a developer of the following formula:

	Normal Developer	Modified Developer
Water, liter	1	1
Benzyl Alcohol, ml	12.64	12.64
NaBr, g	0.417	0.417
NaCl, g	0.730	0.730
Na_2SO_3, g	2.08	2.08
Color Developer CD-3, g	4.17	4.17
Hydroxylaminesulfate, g	2.08	2.08
Methanesulfonamide, g	0	40
Na_2CO_3, g	22.52	0
Sodium sesquicarbonate, g	7.92	0
pH at 70° F	10.0	10.0

Color print papers of the type described in U.S. Patent 2,772,163 were exposed on a Kodak type 1*b* sensitometer and developed in the normal developer shown above. Additional print papers were similarly exposed, but developed in the modified developer. The speed of the papers developed in the modified developer was about four times as fast as those papers developed in the normal developer. This four-fold increase in speed means that only about one-fourth of the exposure is necessary to obtain the same amount of densities if the modified developer is used instead of the normal developer. There was no increase in the amount of fog when the modified developer was used. Thus the methanesulfonamide buffer increased the effective speed of the print paper by about two full *f*-stops without causing any increase in fog, when compared to the normal carbonate buffer.

When the buffers of our invention are used in color photographic processes, the color-forming compounds can be incorporated in the photographic emulsions, as shown in Tong U. S. Patent 2,772,163. Typical color-forming compounds which are primarily useful for use in photographic emulsions are described in Spath U.S. Patent 2,860,976. The buffers of our invention can also be used in color photographic processes where the color couplers are contained in the developing compositions. Typical examples of couplers which are suitable for use in color developers are described in Schwan et al. U.S. Patent 3,068,097.

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.

We claim:

1. A photographic developer composition containing a photographic silver halide developing agent and a water-soluble, non-silver halide reducing sulfonamide buffer.

2. A photographic developer composition containing a photographic silver halide developing agent and a water-soluble, non-silver halide reducing sulfonamide buffer of the following formula:

$$R—SO_2—NH—[(R_1)_{m-1}—NH—SO_2]_{n-1}—R_2$$

wherein m and n each represents a positive integer of from 1 to 2, R_1 represents an alkylene group, R represents a member selected from the class consisting of an alkyl group and an aryl group, and R_2, when n is 1, represents a member selected from the class consisting of a hydrogen atom, an alkyl group and an aryl group, and R_2, when n is 2, represents a member selected from the class consisting of an alkyl group and an aryl group.

3. A photographic developer composition containing a photographic silver halide developing agent and a water soluble, non-silver halide reducing sulfonamide buffer of the following formula:

$$R—SO_2—NH—R_2$$

wherein R represents a member selected from the class consisting of an alkyl group and an aryl group, and R_2 represents a member selected from the class consisting of a hydrogen atom, an alkyl group and an aryl group.

4. A photographic developer composition containing a photographic silver halide developing agent and a buffer represented by the following formula:

$$CH_3—SO_2—NH_2$$

5. A photographic developer composition containing a photographic silver halide developing agent and a buffer represented by the following formula:

$$CH_3—SO_2—NH—C_2H_5$$

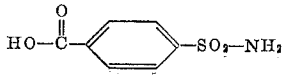
6. A photographic developer composition containing a photographic silver halide developing agent and a buffer represented by the following formula:

$$C_2H_5—SO_2—NH—CH_3$$

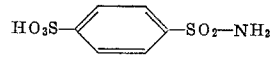
7. A photographic developer composition containing a photographic silver halide developing agent and a buffer represented by the following formula:

$$CH_3—SO_2—NH—C_2H_4—OH$$

8. A photographic developer composition containing a photographic silver halide developing agent and a buffer represented by the following formula:



9. A photographic developer composition containing a photographic silver halide developing agent and a buffer represented by the following formula:



10. A photographic developer composition containing a photographic silver halide developing agent and a water-soluble, non-silver halide reducing sulfonamide buffer of the following formula:

$$R—SO_2—NH—NH—SO_2—R_2$$

wherein R and R_2 each represents a member selected from the class consisting of an alkyl group and an aryl group.

11. A photographic developer composition containing a photographic silver halide developing agent and a buffer represented by the following formula:

$$CH_3—SO_2—NH—NH—SO_2—CH_3$$

12. A photographic developer composition containing a photographic silver halide developing agent and a water-soluble, non-silver halide reducing sulfonamide buffer of the following formula:

$$R—SO_2—NH—R_1—NH—SO_2—R_2$$

wherein R_1 represents an alkylene group, and R and R_2 each represents a member selected from the class consisting of an alkyl group and an aryl group.

13. A photographic developer composition containing a photographic silver halide developing agent and a buffer represented by the following formula:

$$CH_3—SO_2—NH—C_2H_4—NH—SO_2—CH_3$$

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