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(54) Photographic developing solution.

(57) There is described a photographic developing solution which comprises at least one silver halide developing compound, an alkali metal sulphite, sufficient alkali to bring the pH within the range of 8 to 10 and as a buffer a compound of the general formula I:-

$B - R_n$ I

wherein B is a phenol ring or an annelated phenol ring and R is a substituent group other than hydrogen and n is from 1 to 4 such that the compound has a pKa between 8 and 10 and is photographically inert.

Useful compounds of formula I are phenols containing - SO_3H or COOH substituent groups. Particularly useful are the p-substituted compounds.

Another class of compounds of formula I which are particularly useful are naphthol compounds having one or two substituent groups R. Particularly preferred substituent groups R in the naphthol ring system are also -SO_3H and -COOH. An especially useful naphthol compound is 1-naphthol-3,6-disulphonic acid which has a pKa of 8.2. Another useful naphthol compound is 1-naphthol-3-sulphonic acid which has a pKa of 8.6.

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This invention relates to compositions for processing exposed photographic material and in particular to compositions for developing silver halide photographic material.

During the developing of photographic material wherein a latent silver image is converted to a silver image the pH of the developing solution tends to become increasingly acidic. This decrease in pH of the solution slows down the development process greatly. Thus it is usual to add a buffer system or compound to the developing solution.

The pH range for black and white film developers lies in the range 8-10. At the high end of this range, sodium or potassium carbonate are usually used as buffer. Between pH 8 and 9, alkanolamine salts or borax/boric acid are used. However, the latter mixture is becoming more undesirable due to effluent controls by water authorities. Restrictions apply to boron compounds and hence will affect photoprocessors using developers which are formulated with boron containing buffers. Boron and its compounds are toxic in the environment. Thus used processing solutions containing boron may often not be discharged in the normal effluent channels. On the other hand alkanolamine salts contain nitrogen which tends to act as a nutrient for bacterial and algal growth which proliferate greatly using up available oxygen. Thus the use of alkanolamine salts as buffers is also to be deprecated. There is thus a need for a buffer system which does not have the above deleterious effects.

It is the object of the present invention to provide a photographic developing solution which comprises a buffer which is active in the pH range of 8 to 10, which is biodegradable but which does not act as a nutrient for bacteria or algae.

Therefore, according to the present invention there is provided a photographic developing solution which comprises at least one silver halide developing compound, an alkali metal sulphite, sufficient alkali to bring the pH within the range of 8 to 10 and as a buffer a compound of the general formula I:

$$B - R_n \qquad I$$

wherein B is a phenol ring or an annelated phenol ring and R is a substituent group other than hydrogen and n is from 1 to 4 such that the compound has a pKa between 8 and 10 and is photographically inert.

Useful compounds of formula I are phenols containing - SO_3H or COOH substituent groups. Particularly useful are the p-substituted compounds.

Another class of compounds of formula I which are particularly useful are naphthol compounds having one or two substituent groups R. Particularly preferred substituent groups R in the naphthol ring system are also -SO_3H and -COOH. An especially useful naphthol compound is 1-naphthol-3,6-disulphonic acid which has a pKa of 8.2. Another useful naphthol compound is 1-naphthol-3-sulphonic acid which has a pKa of 8.6.

Hydroquinone falls within formula I as set forth and it has a pKa of 9.91 but it can not be used as the only buffer in the developing solution of the present invention as it is photographically active as a developing agent.

The use of a compound of formula I in photographic processing is known, but not where the compound is used as a buffer in the pH range of 8-10. For example in E.P.A. 436027 and US Patent 4569904 compounds of formula I amongst many other compounds are described for use in a method for developing an exposed negative silver halide photographic light-sensitive material, in the presence of a hydrazine derivative, which method comprises treating the material with a developer containing at least components (a) a developing agent, (b) not less than 0.25 mol/liter of a sulfite, and (c) not less than 0.1 mol/liter of a compound having an acid dissociation constant of from $1x10^{-11}$ to $3x10^{-13}$, and having a pH value of from 10.5 to 12.3.

It is stated in USP 4569904 that the presence of a compound similar to that of formula I makes it possible to stably obtain the effects of hydrazines on increasing contrast and sensitivity. According to USP 4569904 these compounds probably act as secondary buffers as in USP 4569904 (column 9), and ordinary buffers such as borax may also be present in the developing solution. Therefore it was very unexpected that the compounds of formula I could be used as the buffering system in a developing solution during the very much lower pH of 8 to 10 rather than the pH of 10.5 to 12.3 cited in USP 4569904.

Preferably the amount of the compound of formula I present in the developing solution of the present invention is from 1 to 40g/litre.

It is to be understood that the compound of formula I must be sufficiently water-soluble to act as a buffer in the developing solution.

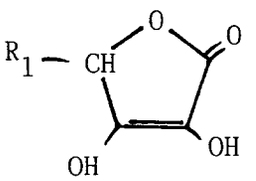
With reference to the phenol compound of formula I, examples of suitable substituents R are -COOH, halides for example -Cl and -SO_3H. However, not all these substituents produce the required pKa in all the p-, m- or o- positions. For example p-hydroxybenzoic acid has a pKa of 9.32, m-hydroxybenzoic acid has a pKa of 9.92 whilst o-hydroxybenzoic acid has a pKa of 13.40. Thus o-hydroxybenzoic acid could not be

used as a buffer in the developing solution of the present invention. M-hydroxybenzoic acid could be used but as it is close to the upper limit of the required pKa range its use is not preferred. On the other hand p-hydroxybenzoic acid has a pKa towards the middle of the required pKa range, is readily soluble in water and has no disadvantageous characteristics such as a strong colour or smell. Thus p-hydroxybenzoic acid is one of the preferred compounds for use as buffer in the developing solution of the present invention.

Another useful compound is p-phenolsulphonic acid which has a pKa of about 9.05. It is to be understood that salts, such as sodium salts, of these acids are equally useful in the present invention.

Any one of the three chloro-substituted phenols could be used as they all have a pKa within the required range but they are not particularly water-soluble and all of them have a strong odour. Thus none of these compounds is preferred as buffering agents in the developing solution of the present invention.

Examples of developing agents which are of use in the photographic developing solutions of the present invention include hydroquinone and substituted hydroquinone which acts as silver halide developing agent and ascorbic acid type compounds which act as silver halide developing agents of the formula II:-



----- II

wherein R_1 is a hydroxylated alkyl group having 1 to 4 carbon atoms or alkali metal salts of such compounds.

Preferably the sulphite present in the developing solution is sodium sulphite. Sodium hydroxide is a suitable alkali to bring the developing solution to the desired starting pH of the freshly prepared developing solution.

Other substances which may be present in the developing solution include sequestering agents such as sodium tripolyphosphate and restraining agents such as sodium bromide. Other components commonly found in photographic processing solutions may also be present.

Example

Five samples of a fine-grain developing solution were prepared. Solution 1 comprised borax, solution 2 comprised p-hydroxybenzoic acid solution 3 comprised p-phenolsulphonic acid solution 4 comprised 1-naphthol-3,6-disulphonic acid, whereas solution 5 contained no buffer.

Solution:	1	2	3	4	5
Metol	1.0g	1.0g	1.0g	1.0g	1.0g
Hydroquinone	2.5g	2.5g	2.5g	2.5g	2.5g
Sodium sulphite	50g	50g	50g	50g	50g
Sodium TPP	1.75g	1.75g	1.75g	1.75g	1.75g
Borax	1.5g	-	-	-	-
p-HBA	-	2.3g	-	-	-
p-PSA	-	-	3.8g	-	-
NDSA	-	-	-	6.0g	-
Water to	1000cc	1000cc	1000cc	1000cc	1000cc

sodium TPP = sodium tripolyphosphate

p-HBA = p-hydroxybenzoic acid

p-HSA = p-phenolsulphonic acid

NDSA = 1-naphthol-3,6-disulphonic acid

The solutions where necessary were adjusted to pH 8.65 using sodium hydroxide.

To test the buffering effect of the compound, photographic silver halide strips were sensitometrically exposed and were developed before, during and after the processing of 0.2m^2 fogged film. In this way, loss

in activity of the developer results in a reduction of pH. In normal situations this loss is compensated for by replenishing the developer thus maintaining pH and component concentration. The area of fogged film chosen is sufficient to reduce the pH of a developing solution containing no buffer to such an extent that it is of no practical use.

The results of the tests were as follows:-

Solution	Film processed (m^2)	Speed (S0.1)	Contrast (G1.5)	pH
1	0	5.68	0.58	8.65
1	0.1	5.64	0.56	-
1	0.2	5.53	0.51	8.55
2	0	5.67	0.62	8.65
2	0.1	5.65	0.60	-
2	0.2	5.52	0.54	8.58
3	0	5.70	0.63	8.65
3	0.1	5.69	0.64	-
3	0.2	5.56	0.56	8.61
4	0	5.65	0.56	8.65
4	0.1	5.63	0.53	-
4	0.2	5.54	0.50	8.61
5	0	5.68	0.55	8.65
5	0.1	5.59	0.52	-
5	0.2	5.48	0.49	8.48

Greater loss of pH in the unbuffered solution is reflected by the largest loss in speed; a loss which would be subjectively very apparent. Smaller losses of speed occur from the buffered solutions where it can be seen that the substituted phenolic compounds (solutions 2 and 3) and substituted naphthol compound (solution 4) provide as much immunity from pH changes as does the borax buffer solution. (solution 1)

Claims

1. A photographic developing solution which comprises at least one silver halide developing compound, an alkali metal sulphite, sufficient alkali to bring the pH within the range of 8 to 10 and which is characterised it comprises as a buffer a compound of the general formula I:-

$B - R_n$ I

wherein B is a phenol ring or an annelated phenol ring and R is a substituent group other than hydrogen and n is from 1 to 4 such that the compound has a pKa between 8 and 10 and is photographically inert.

2. A photographic developing solution according to claim 1 which is characterised in that the amount of the compound of formula I present is from 1g to 40g/litre.

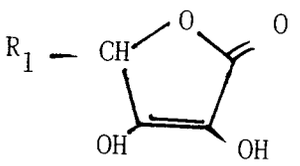
3. A photographic developing solution according to either claim 1 or claim 2 which is characterised in that the compound of formula I is p-hydroxybenzoic acid.

4. A photographic developing solution according to either claim 1 or claim 2 which is characterised in that the compound of formula I is p-phenolsulphonic acid.

5. A photographic developing solution according to either claim 1 or claim 2 which is characterised in that the compound of formula I is 1-naphthol-3, 6-disulphonic acid.

6. A photographic developing solution according to claim 1 which is characterised in that the silver halide developing compound is hydroquinone or a substituted hydroquinone whihc acts as a silver halide developing agent.

7. A photographic developing solution according to claim 1 which is characterised in that the silver halide developing compound is an ascorbic acid type compound of the general formula:-



wherein R_1 is a hydroxylated alkyl group having 1 to 4 carbon atoms or n alkali metal salt of such a compound.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 9091

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	US-A-3 790 383 (I SHIMAMURA ET AL) * claims 1,3-8 * * example 1 * * example 3,table 3,developer N * * column 9, line 22 - line 25 *	1-4,6	G03C5/30 G03C5/305 G03C7/413
A	GB-A-1 367 009 (FUJI PHOTO FILM CO. LTD.) * claims 1-9 * * page 16, line 100 - line 103 * * examples 1,3 *	1-4,6	
A	GB-A-959 563 (KODAK LIMITED) * claims 1-3 * *compound 7 * * page 2, line 96 - line 108 *	1,2,5,6	
A	GB-A-2 139 370 (FUJI PHOTO FILM CO. LTD.) *example 2,run no. 7*	1	
A	PATENT ABSTRACTS OF JAPAN vol. 12, no. 278 (P-738) (3125) 1 August 1988 & JP-A-63 058 444 (FUJI PHOTO FILM CO. LTD.) 14 March 1988 * abstract *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.5) G03C
A	US-A-4 830 948 (T ISHIKAWA ET AL) * column 47, line 60 - column 48, line 30 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 March 1994	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
O : non-written disclosure
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

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