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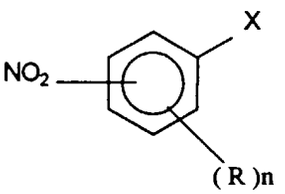
(54) Method for replenishing a color photographic developer

(57) A method for replenishing a color developer containing an antifoggant, the color developer being used intermittently, which comprises adding to the color developer an amount of antifoggant that is not dependent on the intermittent use of the color developer and wherein the antifoggant has the following formula (I)



wherein X is -COOM or -SO_3M with M being hydrogen, an alkali metal or ammonium ion, R is an alkyl group with 1 to 3 atoms of carbon, and n is 0, 1, 2 or 3.

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Description

FIELD OF THE INVENTION

[0001] The present invention concerns a method for replenishing a photographic developer used in the processing of color photographic products, and specifically a method for maintaining the quantity of antifoggant in a developer stable in time by adding to said developer a replenishing solution (also called maintenance or regenerating solution) containing a specific antifoggant.

BACKGROUND OF THE INVENTION

[0002] In the processing of color photographic films, color developers are used that contain as their main constituent a color developing agent in an alkaline medium. These color developers also contain other components such as permeabilizing agents, antifoggants, preservatives, etc.

[0003] The sensitometric characteristics of the processed products depend on the processing parameters: temperature, pH, and concentration of the components. These parameters must therefore be constantly monitored. Also, because the processing itself consumes the components initially present in the baths, these baths must be maintained or replenished. For this purpose the processing manuals propose formulas for replenishing baths, in particular for developers. These replenishing solutions are supplied systematically after the developer has acted for a set number of hours, or every time a set amount of film has been processed in the developer. This replenishing system is fairly problem-free in continuous processing, especially in large plants for the continuous, or practically continuous processing of motion picture film. However, when film processing plants do not operate continuously, but intermittently, for example less than 8 hours a day, the replenishment of the developer is also carried out intermittently, as the developer is used up. Some components of the developer can then decompose between the more widely spaced replenishments. This means that if the processing is intermittent, it is necessary to provide replenishment that will compensate for extra losses due to the decomposition of certain unstable components. This is particularly the case for antifoggants of the dinitrobenzoic acid type. Obviously, the precaution of specifically replenishing when the developer is used intermittently seriously complicates the processing procedure.

[0004] For example, the Manual for Processing Eastman Motion Picture Films, Module 7, Process ECN-2- specifications, EKC, 1990, page 21, gives the following instructions for replenishing the antifoggant n°9 in a developer according to the rate of use:

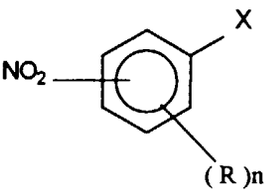
Rate of use hours/day	Quantity of antifoggant g/l
2 or less	0.46
4	0.42
6	0.38
8	0.34
10 or more	0.30

[0005] The usual amount of antifoggant in the developer replenishing solution is 0.30 g/l. When the processing is running again after a stopping, it is necessary to change the replenisher concentration according to the above table. Antifoggant n°9 is a dinitrobenzoic acid, the poor stability of which makes additional specific replenishment necessary if developer use is intermittent. It is found that the more intermittent the developer use is, the more the concentration of antifoggant in the replenishing solution has to be increased. Hence the standard replenishing solution cannot be used if developing is intermittent without incurring a risk of impaired sensitometric characteristics.

SUMMARY OF THE INVENTION

[0006] The object of the present invention is a simplified method of replenishing a color developer that does not suffer from the disadvantages stated above.

[0007] The present invention relates to a method for replenishing a color developer containing an antifoggant, the color developer being used intermittently, which comprises adding to the color developer an amount of antifoggant that is not dependent on the intermittent use of the color developer and wherein the antifoggant has the following formula (I)



wherein X is -COOM or -SO_3M with M being hydrogen, an alkali metal or ammonium ion, R is an alkyl group with 1 to 3 atoms of carbon, and n is 0, 1, 2 or 3.

[0008] The invention also relates to a method of development of an exposed color photographic material that comprises developing the photographic material in an intermittently used developer containing a color developing agent and an antifoggant, and adding to the color developer an amount of the antifoggant that is not dependent on the intermittent use of the color developer, wherein the antifoggant is the antigoggant (I).

DETAILED DESCRIPTION OF THE INVENTION

[0009] Herein the expression "a color developer used intermittently" reflects the fact that in photographic processing laboratories, the processing lines can operate at different rates of use according to the square meter number of film processed daily. Processing laboratories can operate continuously 24 h a day for periods of several weeks or several months or intermittently, a few hours a day or a week.

[0010] In the method of the present invention, the color developer is running intermitendly. With the method of the present invention, it is no more necessary to adapt the amount of antifoggant to be added according to the extend of time the color developer is not running. After a stopping, when the color developer is running again, the added amount per time unit is the same as the added amount before the stopping. It can be thus advantageously a unique replenishing solution containing the antifoggant irrespective of the daily rate of use of the color developer.

[0011] According to one embodiment, the antifoggant amount added to the color developer per running time unit is constant.

[0012] According to one embodiment, the nitro group in formula (I) is positioned meta or para to the COOH or SO_3H group. When n is equal to 1, 2 or 3, R is preferably methyl. In a different embodiment, n is 0 in formula (I), i.e., the benzene ring bears no alkyl group.

[0013] The color developer used in the method of the invention is a conventional color developer usually comprising an alkaline aqueous solution of a color developing agent of the aromatic primary amine type, generally a paraphenylenediamine, for example, 2-amino-5-diethylaminotoluene (known as CD2), 4-amino-N-ethyl-N-(β-methanesulfoamidoethyl)-m-toluidine (CD3), 4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)-aniline (CD4).

[0014] CD2 is generally used in color developers for positive motion picture films, and CD3 is generally used in color developers for negative and intermediate motion picture films. The concentration of the color developing agent is usually at least 7×10^{-3} mol/l, and preferably between 9×10^{-3} and 2×10^{-2} mol/l. This color developer can contain various additives such as sulfite, bisulfite, carbonate, water softener, buffer, wetting agent, accelerator, antifoamant, antibacterial agent, and antifoggant that can be the same as or different from the antifoggant of formula (I). The pH of the color developer is usually between 9 and 12.

[0015] In the scope of the invention, the antifoggant (I) exhibit a redox potential preferably greater than -700 mV, measured relative to an Ag/AgCl/KCl 3M reference electrode. The antifoggant (I) can be 3-nitrobenzoic acid (redox potential -650 mV), 4-nitrobenzoic acid (redox potential -580 mV), 3-nitrobenzenesulfonic acid (redox potential -600 mV), or 4-nitrobenzenesulfonic acid. According to a preferred embodiment, the antifoggant (I) is 3-nitrobenzenesulfonic acid. Given that the antifoggant (I) is incorporated into an alkaline solution, it occurs as a salt of an alkali metal, for example sodium or potassium, or ammonium.

[0016] The color developer can contain an antifoggant working concentration from 2×10^{-4} mole/l and 3×10^{-3} mole/l. The color developer can be prepared from a kit comprising a concentrated alkaline solution (A) containing the antifoggant of formula (I) and a concentrated acidic solution (B) containing the color developing agent of the paraphenylenediamine type, the ready-to-use color developer being obtained by mixing the concentrates (A) and (B) in either order. When the color developer is obtained from concentrated solutions (A) and (B), the volume and antifoggant concentration in the concentrate (A) will be adapted to obtain such a working concentration.

[0017] In the scope of the present invention, the antifoggant (I) can be added to the color developer in powder form. It can be also added in solution form. In a specific embodiment, it can be added through a replenishing solution containing the antifoggant (I). Such a replenishing solution can contain the antifoggant (I) in a concentration from 3×10^{-4} to 5×10^{-3} mole/l.

[0018] The method of this invention can be used in any photographic processing method comprising a color developing step, a bleaching step and a fixing step. The bleaching step and the fixing step can be replaced by a single bleaching-fixing step. One or more washing baths can be inserted between these successive steps. The method of the invention is particularly useful for the processing method of a negative motion picture films such as Eastman Color Negative® sold by Kodak wherein the color developing step is carried out with CD3.

[0019] In the scope of the invention the antifoggant (I) can be added through the replenishing solution. A replenishing solution is a solution continuously added to the color developer in order to compensate the amount of components consumed during the processing of photographic materials. The amount of the replenishing solution to be added can largely vary depending on the component concentration and the processor type. This determination will be easily made by one skilled in the art.

[0020] This invention is illustrated by the following examples:

EXAMPLE 1

[0021] A developer composition as prescribed in the Manual for Processing Eastman Motion Picture Films, Module 7, Process ECN-2-specifications, EKC, 1990, page 21 was prepared.

Water at 27°C	800 ml
Kodak n°4 water softener	2.0 ml
Anhydrous sodium sulfite	2.0 g
Antifoggant n°9 (3,5-dinitrobenzoic acid)	0.22 g
Anhydrous sodium bromide	1.20 g
Anhydrous sodium carbonate	26.6 g
Sodium bicarbonate	2.7 g
Kodak CD3 developer	4.0 g
Water qsp	1 liter
pH at 25°C	10.23

[0022] An accelerated stability test was performed. For this test, the above freshly prepared developer was placed in a plastic bottle and stored at 50°C during 24 days. The sample of the developer was analysed after 3, 9, 16 and 24 days in order to determine the remaining amount of antifoggant.

[0023] The amount of remaining antifoggant versus time is reported in table I below (expressed in weight %).

EXAMPLE 2

[0024] A color developer containing the components as disclosed in example 1 was prepared except that the 3,5-dinitrobenzoic acid was replaced by 0.173 g/l of 3-nitrobenzoic acid. The stability test of the example 1 was performed on this color developer containing 3-nitrobenzoic acid. The results of the stability test are given in Table I below.

EXAMPLE 3

[0025] A color developer containing the components as disclosed in example 1 was prepared except that the 3,5-dinitrobenzoic acid was replaced by 0.173 g/l of 4-nitrobenzoic acid. The stability test of the example 1 was performed on this color developer containing 4-nitrobenzoic acid. The results of the stability test are given in Table I below.

EXAMPLE 4

[0026] A color developer containing the components as disclosed in example 1 was prepared except that the 3,5-dinitrobenzoic acid was replaced by 0.233 g/l of 3-nitrobenzenesulfonic acid. The stability test of the example 1 was performed on this color developer containing 3-nitrobenzenesulfonic acid. The results of the stability test are given in Table I below.

TABLE I

Duration of storage (days)	Amount of remaining antifoggant (weight %)			
	Ex 1 (Comp.)	Ex 2	Ex 3	Ex 4
0	100	100	100	100
3	72	100	100	100
9	35	100	98	100
16	9	98	98	100
24	1	98	95	98

[0027] These results show that, the amount of antifoggant (I) being time stable, it is no more necessary to add to the developer an amount of antifoggant (I) dependent on the intermittent use of the developer. These examples show that when the developer containing the antifoggant (I) is used, the amount of antifoggant to be added will only dependent on the component consumption by the photographic elements processed. This is not dependent on the intermittent use of the color developer.

EXAMPLE 5

[0028] The same test was performed on a seasoned color developer containing the components as disclosed in example 1 was prepared except that the 3,5-dinitrobenzoic acid was replaced by 3-nitrobenzenesulfonic acid. The stability test of the example 1 was performed during 10 days in the experimental condition of the example 1. The results of the stability test are given in Table II below.

TABLE II

	Concentration in the seasoned developer
T = 0	0.356 g/l
T = 10 days	0.358 g/l

[0029] These results show that with an intermittently used developer, the antifoggant (I) in a seasoned developer avoids any change in the amount to be added even after stopping the processing during 10 days.

EXAMPLE 5

[0030] This example is carried out with a Photomec machine wherein the color developer is as disclosed below. The color developer is replenished with a replenishing solution as disclosed below and containing 3-nitrobenzenesulfonic acid as antifoggant. The volume of the color developer is carried on through an overflow.

[0031] The color developer and the replenishing solution have the following compositions:

	Developer	Replenishing solution
Water at 27°C	800 ml	800 ml
Kodak n°4 water softener	2.0 ml	2.7 ml
Anhydrous sodium sulfite	2.0 g	2.5 g
3-nitrobenzenesulfonic acid	0.35 g	0.48 g
Anhydrous sodium bromide	1.20 g	0.93 g
Anhydrous sodium carbonate	25.6 g	25 g
Sodium bicarbonate	2.7 g	0.6 g
Kodak CD3 developer	3.9 g	5.1 g
Water qsp	1 liter	1 liter

(continued)

	Developer	Replenishing solution
pH at 25°C	10.23	10.25

[0032] After a running time, a sample of the seasoned developer was taken at the outlet of the overflow from the developing tank, just before stopping the processing line. This sample contained 0.360 g/l of antifoggant (I). Another sample of the same developer was taken after 70 hours with the line idle, just before starting it up again. The developer was not replenished during the stopping of the processing line. The antifoggant content in the second sample was 0.358 g/l.

[0033] This test reproduced the conditions of an intermittent operation of the processing, and it shows that the concentration of antifoggant has not changed. Replenishing of the developer can therefore be carried out using the same solution as the replenishing solution used before stopping the processing. This was not the case when 3,5-dinitrobenzoic acid was used as antifoggant, as disclosed in Manual for processing Eastman motion picture Films, module 7, Process ECN-2 specifications, EKC, 1990, page 21.

EXAMPLE 6

[0034] In this example a ready-to-use developer and a replenishment solution were prepared with the composition specified in example 5:

[0035] An Eastman Color Intermediate 5274® negative color film was exposed through a step tablet with 21 density steps, each of these steps having an increment of 0.15 LogE with an exposure light of a color temperature 2850 K and an illuminant D1, for 1/50 sec. The film was developed using photographic process ECN-2®, which comprises the developer prepared in example 3, a bleaching bath, a fixing bath, and a final washing bath, both the film and the process being commercialized by Kodak, and the developer was maintained using the replenishing solution specified in example 1.

[0036] By reading in the three colors blue, green and red on a densitometer, the following sensitometric results were obtained (seasoned bath). The results are reported in the table below.

[0037] The same experiment was conducted with a color developer and a replenisher containing 3,5-dinitrobenzoic acid, in the conditions specified in the Manual for processing Eastman motion picture Films. The results are reported in the table below (..).

	Red-sensitive layer	Green-sensitive layer	Blue-sensitive layer
Dmin (+ 0.04)	0.178 **(0.176)**	0.600 **(0.594)**	0.958 **(0.96)**
Dmax (+ 10)	1.40 **(1.399)**	2.03 **(2.035)**	2.32 **(2.33)**
Contrast (+ 0.04)	0.530 **(0.532)**	0.576 **(0.581)**	0.564 **(0.572)**
Speed (+ 4)	516.5 **(516.1)**	527.8 **(527.2)**	514.6 **(514.)**

Dmin = minimal density corresponding to a portion of the unexposed film (support + fog)

Dmax = maximal density of the film.

Speed = 100(3-LogE), where E is the exposure at the point of density Dmin + 1.

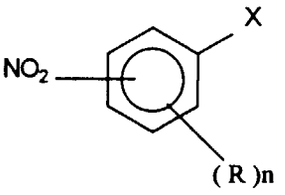
Contrast = slope of the straight line between the point of density Dmin + 0.20 and that of exposure greater than 1.35 LogE.

[0038] This shows the efficiency of the method of the invention as regard to the sensitometric results.

[0039] The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

1. A method for replenishing a color developer containing an antifoggant, the color developer being used intermittently, which comprises adding to the color developer an amount of antifoggant that is not dependent on the intermittent use of the color developer and wherein the antifoggant has the following formula (I)



wherein X is -COOM or -SO_3M with M being hydrogen, an alkali metal or ammonium ion, R is an alkyl group with 1 to 3 atoms of carbon, and n is0, 1, 2 or 3.

2. The method of claim 1 wherein the antifoggant amount added to the color developer per running time unit is constant.

3. The method of claim 1 wherein the added amount of the antifoggant is such that the color developer concentration is between 2 x 10^{-4} and 3 x 10^{-3} mole/l.

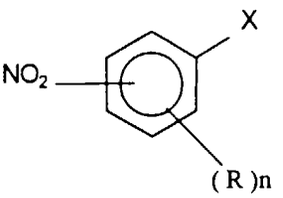
4. The method of claim 1 wherein the antifoggant amount is added to the color developer through a replenishing solution.

5. The method according to claim 1 wherein the nitro group in the formula (I) is positioned meta or para to the COOH or SO_3H group.

6. Method according to any of claims 1 or 2, wherein n is equal to 0 in the formula (I).

7. Method of development of an exposed color photographic material that comprises:

developing the photographic material in an intermittently used developer containing a color developing agent and an antifoggant, and
adding to the color developer an amount of the antifoggant that is not dependent on the intermittent use of the color developer, wherein the antifoggant has the following formula (I)



wherein X is -COOM or -SO_3M with M being either an atom of hydrogen, or an alkali metal or ammonium ion, R is an alkyl group with 1 to 3 atoms of carbon, n is 0, 1, 2 or 3.

8. The method of claim 6 wherein the antifoggant is added to the color developer through a replenishing solution having an antifoggant concentration from
3 x 10^{-4} to 5 x 10^{-3} mole/l.

9. Use of an antifoggant having formula (I) as defined in Claim 1 for providing a developer having a stable amount of antifoggant agent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 42 0030

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.7)
X Y	JP 60 052849 A (FUJI) 26 March 1985 (1985-03-26) * page 2, left-hand column; examples 8,9 * * page 3, left-hand column, line 4 - line 11 * * page 3, left-hand column, line 21 - line 26 * * page 7, right-hand column, line 17 *	1-3,6,7,9 4,8	G03C7/44
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X Y	GB 1 468 015 A (MAY & BAKER) 23 March 1977 (1977-03-23) * page 2, line 17 - line 64; claim 1 *	1-3,6,7,9 4,8	
Y	US 5 063 141 A (NAKAMURA) 5 November 1991 (1991-11-05) * column 14, line 17 - line 19 *	4,8	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 March 2000	Magrizos, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 42 0030

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