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B-2640 Mortsel(BE)**(54) **An ascorbic acid type developer with a particular composition.**

(57) A developer solution for the development of photographic silver halide materials is disclosed comprising (1) an ascorbic acid type developing agent, and (2) a mixture of at least two 3-pyrazolidone type developing agents chosen from (a) 1-phenyl-3-pyrazolidone, (b) 1-phenyl-4-methyl-3-pyrazolidone, (c) 1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone, (d) 1-phenyl-4,4'-dimethyl-3-pyrazolidone.

In a preferred embodiment the ascorbic acid type developing agent is l-ascorbic acid or iso-ascorbic acid or a salt thereof, and the mixture of the 3-pyrazolidones consists of a mixture of 1-phenyl-3-pyrazolidone and 1-phenyl-4-methyl-3-pyrazolidone. The developer composition of the invention shows improved sensitometric stability against a pH decrease caused by exhaustive continuous processing without developer replenishment.

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1. Field of the invention.

The present invention relates to the field of photographic developing solutions and more particularly to a photographic developing solution having a particular combination of developing agents.

2. Background of the invention.

In general, the processing of black-and-white silver halide photographic materials is performed in the order of development, fixing and washing. Development is commonly carried out with aqueous alkaline developer compositions containing a developing agent, usually of the dihydroxybenzene type such as hydroquinone.

Due to the toxicity and environmental hazards posed by the use of hydroquinone, several substitutes which are less toxic by nature have been proposed. For example the developing activity of ascorbic acid and some chemical analogues is known for quite some time in the photographic art. However ascorbic acid and derivatives are regarded as rather weak developers in the pH-range in which hydroquinone acts as a developing agent. Hence, since the first report of the developing activity of iso-ascorbic acid and its optical isomer in *Berichte*, Vol.67, p.1239 (1934) by Mauer et al., there have been several publications on developers containing a superadditive combination of a conventional developing agent and an ascorbic acid derivative used as auxiliary developer. So, US 2,688,549 discloses the combination of a 3-pyrazolidone developing agent and of an ascorbic acid derivative. GB 1,266,533 describes the combination of a p-hydroxybenzene developing agent, an ascorbic acid and sulphite ions. An equally good developing activity for both surface and internal latent images is claimed in US 3,826,654 which discloses a combination of a 3-pyrazolidone, an ascorbic acid, a heterocyclic thione or thiol and an alkali iodide at a pH of at least 12.

However developing solutions containing ascorbic acid derivatives which are themselves excellent antioxidants have poor resistance against air oxidation and can not be left in continuous transport automatic processors for several days without undergoing a dramatic decrease in developing activity. This decrease in developing activity is mainly due to the decrease of the pH. The continuous contact of these solutions with oxygen of the air consumes an amount of developing agent and will lead in the case of ascorbic acid derivatives to a pH decrease. Developing silver on the other hand consumes also an amount of developing agent leading also to a pH decrease.

Thus, in continuous automatic processing, especially in the case without replenishment by fresh developer, a gradual pH decrease will always occur, resulting in a less active developing system causing severe lowering of sensitivity and gradation for a given constant development time. However it is evident that this is a very undesirable situation and that a solution has to be sought for minimizing these adverse effects.

It is an object of the present invention to provide a photographic developing solution containing an ascorbic acid type developing agent, the development activity of which is only moderately affected by the pH decrease resulting from continuous processing without replenishment.

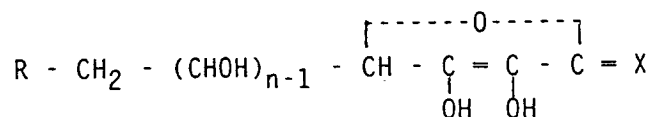
It is a further object of the present invention to provide a method for developing an image-wise exposed silver halide emulsion layer to a black-and-white image using such a particular developing solution.

3. Summary of the invention.

The objects of the present invention are realized by providing a developing solution comprising :

(1) an ascorbic acid type developing agent corresponding to general formula (I), or a salt of it :

(I)



wherein X represents an oxygen atom or an imino group, and

n represents a positive integer from 1 to 4, and

R represents a hydroxy group when n is 1, and R represents a hydroxy group or a hydrogen atom when n is 2 to 4.

(2) a mixture of at least two 3-pyrazolidone type developing agents chosen from the group consisting of:

- (a) 1-phenyl-3-pyrazolidone ("Phenidone", P),
- (b) 1-phenyl-4-methyl-3-pyrazolidone ("methyl-Phenidone", MP),
- (c) 1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone ("methyl-hydroxymethyl-Phenidone", MHMP),
- (d) 1-phenyl-4,4'-dimethyl-3-pyrazolidone ("dimethyl-Phenidone", DMP).

It was surprisingly found that the use of particular mixtures of two Phenidone type auxiliary developing agents in combination with an ascorbic acid type main developing agent caused substantially less sensitometric deterioration, namely sensitivity and gradation loss, due to pH decrease, than when only one Phenidone type auxiliary developing agent was present. In a preferred embodiment the ascorbic acid type developing agent is L-ascorbic acid or iso-ascorbic acid, or a salt thereof, and the mixture of the at least two Phenidone type agents consists of a mixture 1-phenyl-3-pyrazolidone (P) and 1-phenyl-4-methyl-3-pyrazolidone (MP).

4. Detailed description of the invention.

Preferred ascorbic acid type developing agents according to general formula (I) for use in accordance with the present invention are L-ascorbic acid and iso-ascorbic acid. Other useful compounds include imino-L-ascorbic acid, 6-desoxy-L-ascorbic acid, L-rhamnoascorbic acid, L-fucoascorbic acid, D-glucoheptoascorbic acid, D-glucoascorbic acid, L-erythroascorbic acid, and their stereoisomers. The developing agents can be incorporated in the developing solution in the free acid form or as a salt, preferably an alkali salt.

The ascorbic acid type developing agent is incorporated in the developer in a concentration ranging preferably between 0.1 and 0.6 mole/liter, corresponding to a range between 25 and 100 g/l for ascorbic acid.

The at least two 3-pyrazolidone type auxiliary agents are chosen from the group consisting of (a) 1-phenyl-3-pyrazolidone ("Phenidone", P), (b) 1-phenyl-4-methyl-3-pyrazolidone ("methyl-Phenidone", MP), (c) 1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone ("methyl-hydroxymethyl-Phenidone", MHMP), (d) 1-phenyl-4,4'-dimethyl-3-pyrazolidone ("dimethyl-Phenidone", DMP). In a preferred embodiment a mixture of two is chosen and the most preferred choice consists of a mixture of 1-phenyl-3-pyrazolidone ("Phenidone", P) and 1-phenyl-4-methyl-3-pyrazolidone ("methyl-Phenidone", MP) as will become clear from the examples. In this embodiment the preferred concentration of 1-phenyl-3-pyrazolidone ranges from 0.1 to 2.0 g/l, and the preferred concentration of 1-phenyl-4-methyl-3-pyrazolidone ranges from 0.1 to 5.5 g/l.

The developing solution can further contain an anti-fogging agent. Many known compounds can be added as fog-inhibiting agent or stabilizer to a processing solution. Suitable examples are e.g. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione and oxazoline-thione. Other classes include triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JA-Appl. 75-39537, and GB 1,500,278 and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide compounds. A preferred compound for use in accordance with the present invention is 1-phenyl-5-mercaptotetrazole.

The developing solution according to the present invention preferably further contains a compound providing halide ions as development rate regulator, most preferably sodium or potassium bromide in a concentration between 0.01 and 0.2 mole/liter. Further sulphite ions can be present as antioxidant preferably as an alkali sulphite in a concentration between 0.1 and 0.8 mole/liter.

The alkali agent for establishing the start pH of the developer is preferably sodium or potassium hydroxide.

The developing solution can further contain buffering agents. Suitable buffer systems include carbonate buffer, phosphate buffer, metaborate buffer, etc. The concentration of these buffering agents is preferably about 0.4 mole/liter.

Other adjuvants well known to those skilled in the art can be incorporated into the developer solution. A survey of conventional developer addenda is given by Grant Haist in "Modern Photographic Processing" - John Wiley and Sons - New York (1979) p. 220-224. Examples of such addenda include complexing agents for calcium and magnesium ions, present in hard water, e.g. ethylenediaminetetraacetic acid and analogous compounds. Further can be present anti-foaming agents, surface-active agents, biocides, thickening agents like polystyrene sulphonate and antioxidants like benzoate and cyclodextrine. The developing liquid can contain so-called anti-sludge agents in order to reduce

dirt streaks on developed photographic material. Finally the solution can contain development accelerating agents like polyalkyleneoxides and alkanolamines and hardening agents including latent hardeners.

The scope of the present invention further comprises a method for developing an image-wise exposed photographic material by means of the described developing solution. The method of the present invention is especially useful when no replenisher solution is present for compensating the pH drop during exhaustive continuous processing.

After development a conventional fixing step, washing step and drying step are performed. Preferably an automatically driven processing apparatus is used.

The silver halide photographic materials which can be processed by the method of the present invention include all kinds of black-and-white materials, e.g. films and papers for amateur photography, films for cinematography, materials for radiographic recording and materials for graphic arts. The silver halide emulsions present as photosensitive element in those photographic materials can be of any known halide composition, e.g. bromide, chloride, iodobromide, chlorobromide or chloriodobromide emulsions. The best results with the present invention are however obtained with materials containing emulsions rich in bromide, and more particularly with emulsions containing at least 70 mole % of bromide.

The following examples illustrate the present invention without however limiting it thereto.

EXAMPLES

Example 1

A silver halide material for microfilm application having a silver halide coverage equivalent to 3.6 g of silver nitrate per sq.m. and containing a 100% silver bromide emulsion with an average grain size of 0.3 micron was processed in a automatic processor, having a tank solution of 1 liter. The decrease in development activity due to the pH decrease on exhaustive processing was simulated by comparing the sensitometry in two solutions, one adjusted to pH 10.5, the other to pH 9.9. The development time applied was 20 s and the temperature was kept constant at 38 °C. The basic composition of these developer solutions was :

Water	600 ml
K ₂ SO ₃	65 g
K ₂ CO ₃	61 g
KBr	15 g
Ascorbic acid sodium salt	50 g
KOH	8.5 g (pH 9.90)
or	
KOH	16.5 g (pH 10.50)
Water to make	1 l.

The following derivatives of 3-pyrazolidone were added in amounts according to table 1 : 1-phenyl-3-pyrazolidone (P), 1-phenyl-4-methyl-3-pyrazolidone (MP) and 1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone (MHMP) and several mixtures of these compounds. Table I shows the effects of these compounds and of their combinations on the sensitivity (SENS, measured at density 1.1 + Dmin) and on the gradation in the toe of the sensitometric curve (GRAD_t, measured between densities 0.1 + Dmin and 1.1 + Dmin). In this table the difference of these parameters (DSENS, DGRAD_t) when changing the pH from 10.5 to 9.9 is also shown.

TABLE 1

	P (g/l)	MP (g/l)	MHMP (g/l)	pH=10.50 SENS*	GRAD _t	PH=9.90 SENS	GRAD _t	pH 10.5->9.9 DSSENS	DGRAD _t
5	0.5	-	-	125	1.86	116	1.71	-9	-0.15
10	1.5	-	-	139	1.95	130	1.76	-9	-0.19
	-	1	-	133	1.96	114	1.61	-19	-0.35
	-	2.5	-	144	1.92	134	1.82	-10	-0.10
	-	-	2	132	1.92	117	1.64	-15	-0.28
15	-	-	4	140	1.94	132	1.81	-8	-0.13
	0.5	1	-	136	2.04	132	1.93	-4	-0.11
	1.5	2.5	-	141	1.96	139	1.92	-2	-0.04
	0.5	-	2	138	1.96	126	1.81	-12	-0.15
20	1.5	-	4	145	1.95	139	1.89	-6	-0.06
	-	1	2	137	1.95	128	1.81	-9	-0.14
	-	2.5	4	149	1.92	138	1.81	-11	-0.11

25 * : SENS = sensitivity expressed as relative log Et, one unit being 0.01 log Et ; higher figure means higher sensitivity.

30 The results of table 1 show that the combinations of two Phenidone type developing agents give better results than their separate application. The combination of 1-phenyl-3-pyrazolidone (P) and 1-phenyl-4-methyl-3-pyrazolidone (MP) shows the best result, i.e. the lowest decrease of sensitivity and gradation when changing the pH from 10.50 to 9.90.

35 Example 2

The goal of the tests described in this example was to optimize the ratio of the amounts of P and MP, which proved to be the best combination according to example 1. The microfilm material used was similar as the one used in example 1. The basic composition of the developing solutions was the same as the composition of example 1. Table 2 shows the results of using different ratio's of P and MP.

TABLE 2

	P (g/l)	MP (g/l)	pH = 10.50		PH = 9.90		pH 10.5->9.9	
			SENS	GRAD _t	SENS	GRAD _t	DSSENS	DGRAD _t
45	0.5	1.0	138	1.93	127	1.77	-11	-0.16
	0.5	1.5	142	1.92	133	1.81	-9	-0.11
	0.5	2.0	141	1.91	138	1.88	-3	-0.03
50	1.0	1.0	143	1.95	134	1.81	-9	-0.14
	1.0	1.5	145	1.95	136	1.84	-9	-0.11
	1.0	2.0	145	1.94	140	1.89	-5	-0.05
	1.5	1.0	145	1.94	138	1.86	-7	-0.08
	1.5	1.5	147	1.95	141	1.91	-6	-0.04
55	1.5	2.0	147	1.94	142	1.89	-5	-0.05
	2.0	2.5	149	1.89	141	1.85	-8	-0.04

Table 2 shows that several ratio's of P and MP gave good results, namely low decrease of sensitivity and toe gradation for a change of pH from 10.50 to 9.90. The combination of 0.5 g/l of 1-phenyl-3-pyrazolidone (P) and 2 g/l 1-phenyl-4-methyl-3-pyrazolidone (MP) was the best but the ratio proved to be not critical.

Example 3

The same silver bromide film and the same basic developing solution as described in example 1 were used. The development proceeded at 5 different developing times. In one developer, 1.5 g/l 1-phenyl-3-pyrazolidone (P) was added and in the other 0.5 g/l 1-phenyl-3-pyrazolidone (P) together with 1 g/l 1-phenyl-4-methyl-3-pyrazolidone (MP) was used. Table 3 shows the change in sensitivity ($1.1 + D_{min}$), change in toe gradation ($DGRAD_t$) (measured between $0.1 + D_{min}$ and $1.1 + D_{min}$) and change in straight part gradation ($DGRAD$) (measured between $0.5 + D_{min}$ and $1.5 + D_{min}$) when the pH of developer was decreased from 10.50 to 9.90.

TABLE 3

	time (s)	DSSENS	$DGRAD_t$	DGRAD
1.5 g/l P	14	-10.0	-0.18	-0.315
	18	-6.0	-0.13	-0.15
	22	-8.5	-0.13	-0.14
	26	-4.5	-0.08	-0.16
	30	-3.5	-0.11	-0.11
0.5 g/l P + 1 g/l MP	14	-9.0	-0.145	-0.27
	18	-1.0	-0.2	+0.015
	22	-1.5	-0.03	+0.04
	26	-1.0	-0.07	+0.04
	30	-1.5	-0.08	+0.07

For the same amount of 3-pyrazolidone derivatives (this is molar even less), the decrease of the sensitometric values was much less for the combination of the two developing agents in comparison to the use of 1-phenyl-3-pyrazolidone alone, at least at developing times greater than 14 s. Moreover, the gradation measured between $0.5 + D_{min}$ and $1.5 + D_{min}$, was even slightly increased when lowering the pH from 10.50 to 9.90.

Example 4

The same silver bromide film as described in example 1 and 3 and a similar developing solution as described in example 1 was used. This time the basic developer composition was adjusted to pH 10.70. In the first developer, 0.5 g/l 1-phenyl-3-pyrazolidone (P) together with 2 g/l 1-phenyl-4-methyl-3-pyrazolidone (MP) was added. In the second developer, 2.35 g/l of 1-phenyl-3-pyrazolidone (P) alone was added, corresponding to an equimolar amount of developer as in the first developer. In the third developer, an equimolar amount of 1-phenyl-4-methyl-3-pyrazolidone (MP) alone, corresponding to 2.35 g/l, was added. The development was performed in a low volume processor at 38 °C in 20 s.

In each developer, 9 m²/l film was processed, without replenishment by fresh developer. The pH decreased in all cases from 10.70 to 9.92. Table 4 shows the sensitometric results after processing of respectively 0, 3, 6 and 9 m²/l film : minimum density (D_{min}), sensitivity (SENS) (measured at $1.1 + D_{min}$) and toe gradation ($GRAD_t$) (measured between 0.1 and $1.1 + D_{min}$).

TABLE 4

	m2/l	Dmin	SENS	GRAD _t
Developer 1: 0.5 g/l P 2 g/l MP	0	8	135	1.81
	3	8	134	1.77
	6	8	131	1.76
	9	8	120	1.58
Developer 2: 2.35 g/l P	0	9	139	1.79
	3	9	131	1.63
	6	9	126	1.59
	9	10	121	1.53
Developer 3: 2.55 g/l MP	0	11	138	1.74
	3	10	128	1.65
	6	10	122	1.56
	9	9	113	1.43

The results show that a mixture of 0.5 g/l 1-phenyl-3-pyrazolidone (P) together with 2 g/l 1-phenyl-4-methyl-3-pyrazolidone (MP) (developer 1) is preferable above an equimolar amount of 1-phenyl-3-pyrazolidone (2.35 g/l P ; developer 2) alone or an equimolar amount of 1-phenyl-4-methyl-3-pyrazolidone (2.55 g/l MP ; developer 3) alone. Developer 1 showed a lower decrease of sensitivity and toe gradation and moreover gave rise to a lower Dmin in comparison with developer 2 and 3.

Example 5

The same silver bromide film and the same basic developing solution as described in example 1 were used. The decrease in development activity due to the pH decrease on exhaustive processing was simulated by comparing the sensitometry in two solutions, one adjusted to pH 10.5, the other to pH 9.9. The development time applied was 20 s and the temperature was kept constant at 38 °C. The following derivatives of 2-pyrazolidone were added in amounts according to table 5 : 1-phenyl-3-pyrazolidone (P) and 1-phenyl-4,4'-dimethyl-3-pyrazolidone (DMP). Table 5 shows the effects of these compounds and of their combinations on the change in sensitivity (DSENS, measured at density 1.1 + Dmin), on the change of gradation in the toe of the sensitometric curve (DGRAD_t, measured between densities 0.1 + Dmin and 1.1 + Dmin) and on the change of gradation (DGRAD, measured between densities 0.5 + Dmin and 1.5 + Dmin) when changing the pH from 10.5 to 9.9.

TABLE 5

P (g/l)	DMP (g/l)	DSENS	DGRAD _t	DGRAD
0.5	0	- 4.5	- 12.5	- 13
1.5	0	- 5.5	- 6.5	- 8
0	0.5	- 11.5	- 14.5	- 7.5
0	1	- 13	- 20	- 20.5
0.5	0.5	- 4	- 7	- 4
0.5	1	- 4.5	- 5	- 2
1.5	0.5	- 2.5	- 13.5	- 15
1.5	1	- 2	- 1.5	- 0.5

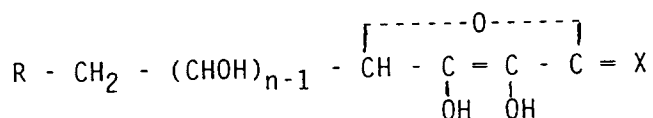
The results of table 1 show that the combination of 1-phenyl-3-pyrazolidone (P) and 1-phenyl-4,4'-dimethyl-3-pyrazolidone (DMP) give better results than their separate application, as was also found in example 1. The best results are obtained with 1.5 g/l P in combination with 1 g/l DMP.

Claims

1. Photographic developing solution comprising :

(1) an ascorbic acid type developing agent corresponding to general formula (I), or a salt of it :

(I)



wherein X represents an oxygen atom or an imino group, and

n represents a positive integer from 1 to 4, and

R represents a hydroxy group when n is 1, and R represents a hydroxy group or a hydrogen atom when n is 2 to 4.

(2) a mixture of at least two 3-pyrazolidone type developing agents chosen from the group consisting of :

- (a) 1-phenyl-3-pyrazolidone,
- (b) 1-phenyl-4-methyl-3-pyrazolidone,
- (c) 1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone,
- (d) 1-phenyl-4,4'-dimethyl-3-pyrazolidone.

2. Developing solution according to claim 1 wherein said ascorbic acid type developing agent is l-ascorbic acid or iso-ascorbic acid or a salt thereof.

3. Developing solution according to claim 1 or 2 wherein said ascorbic acid type developing agent is present in a concentration between 0.1 and 0.6 mole/l.

4. Developing solution according to any of claims 1 to 3 wherein said mixture of at least two 3-pyrazolidone type developing agents is a mixture of 1-phenyl-3-pyrazolidone and of 1-phenyl-4-methyl-3-pyrazolidone.

5. Developing solution according to claim 4 wherein said 1-phenyl-3-pyrazolidone is present in a concentration between 0.1 and 2.0 g/l, and said 1-phenyl-4-methyl-3-pyrazolidone is present in a concentration between 0.1 and 5.5 g/l.

6. Method for developing an image-wise exposed photographic material, comprising a support and a silver halide emulsion layer, by means of a developer solution according to any of claims 1 to 5.

7. Method according to claim 6 wherein there is no replenisher for said developing solution.

8. Method according to claim 6 or 7 wherein the silver halide emulsion, present in said silver halide layer, contains at least 70 mole % of bromide.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 20 2545

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL5)
Y	US-A-5 041 363 (HARUHIKO SAKUMA) * claims 1,8,9 * ---	1-6	G03C5/30 G03C5/305
Y	GB-A-2 011 103 (AGFA-GEVAERT N.V.) * page 2, line 28 - line 40; claim 1 * ---	1-4,6	
Y	US-A-5 098 819 (AUDENRIED W. KNAPP) * the whole document * ---	1-6	
Y	FR-A-1 108 865 (KODAK-PATHÉ) * page 5, line 46 - page 6, line 12; example 6 * -----	1-6	
			TECHNICAL FIELDS SEARCHED (Int.CL5)
			G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13 December 1993	Examiner Hindia, E
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			