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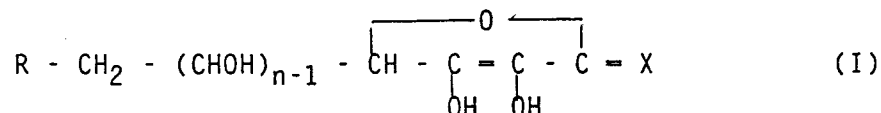
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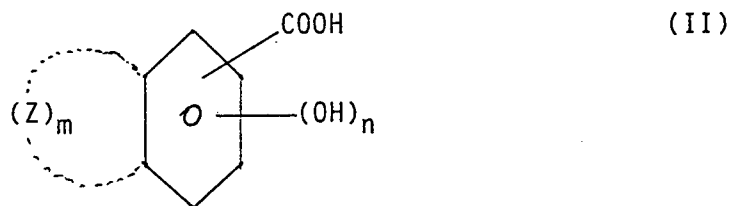
54 **Stabilized ascorbic acid developer.**

57 A silver halide developing solution is provided characterized by a pH of at least 12.0 and containing :
- (a) a sugar derivative or an alkali metal salt thereof, present in a concentration of more than 0.4 mole/liter and corresponding to following general formula (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.

- (b) a compound corresponding to general formula (II), or an alkali metal salt thereof :



wherein Z represents the necessary atoms to form a benzocondensed ring, m = 0 or 1, and n = 1, 2 or 3.
Preferred sugar derivatives corresponding to general formula (I) are l-ascorbic acid and iso-ascorbic acid.
A preferred compound according to general formula (II) is salicylic acid.

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1. Field of the invention.

The present invention relates to photographic developers and more particularly to ascorbic acid developers showing improved stability.

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2. Background of the invention.

In graphic and reprographic arts the accurate sharp reproduction of line edge and screen dot originals is of uttermost importance. This goal is reached by the combination of specially designed graphic arts materials and appropriate processing systems producing so-called "lith quality". A first group of such processing systems consists of the traditional "lith developers" characterized by the presence of hydroquinone as the sole developing agent and a low sulphite ions content giving rise to an infectious development mechanism. However these conventional developers are rather instable in time and require complicated regeneration systems for both oxidation and exhaustion. In more recent times so-called "hard dot Rapid Access" developers were introduced on the market which combine a good stability with a "lith quality" in the reproduction of edges and screen dots. Examples of such developers and corresponding appropriate photographic materials include the GRANDEX system, marketed by FUJI PHOTO Ltd, AG-FASTAR, marketed by ADFA-GEVAERT N.V. and the ULTRATEC system, marketed by EASTMAN KODAK Co.

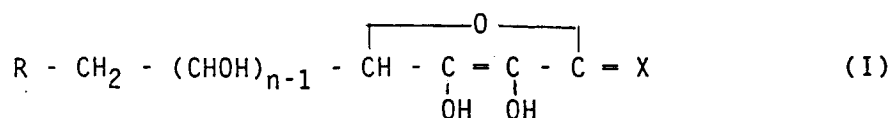
However all these developer systems show some disadvantages from an ecological or toxicological point of view. E.g. hydroquinone is a rather unwanted ingredient because of its allergenic effects. The biodegradation of disposed Phenidone is too slow. Sulphite ions show a high COD (Chemical Oxygen Demand) and the resulting sulphate ions are harmful for e.g. concrete. As a consequence it is undesirable that depleted solutions of this kind would be discharged into the public sewerage; they have to be collected and destroyed by combustion, a cumbersome and expensive process. As a consequence residual solutions containing sulphite produce emissions containing sulphurdioxide and/or sulphurtrioxide on combustion. On the other hand, some "hard dot Rapid Access" systems are ecologically suspect due to the presence of hydrazine or hydrazide derivatives and/or the presence of amino compounds which can be toxic or too volatile as stated in US 4,975,354. It is possible that unwanted organic solvents are used in order to introduce some water insoluble compounds into the photographic material. Some of these suspect compounds can be washed out partially on development. So there is a permanent need for developing solutions which can be disposed of in a safer way for the environment and which are more consumer-friendly.

A class of developing agents which can be concerned in this connection is formed by ascorbic acid and analogous compounds.

The developing activity of l-ascorbic acid (vitamine C) and some chemical analogues is known since many years in the photographic art. In their report on the synthesis of iso-ascorbic acid (iso-vitamine C or d-arabo-ascorbic acid) in *Berichte*, Vol.67, p. 1239 (1934) Maurer at al. for the first time report tests on ascorbic acid and its optical isomer as developers for a photographic plate and describe them as active developers. Later on several publications on developers disclose a superadditive combination of a conventional developing agent and an ascorbic acid derivative used as auxiliary developer or as an antioxidant. 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.

In his study on the mechanism of lith development, published in *J. Phot. Sci.* Vol. 27 (1979), p. 185, Zwicky shows that a lith effect can occur with ascorbic acid as the sole developing agent and he illustrates the effect with photographs showing reproduced line edges and contact screen dots. The developing solution employed contained 112 g of ascorbic acid per liter, potassium bromide, formaldehyde bisulphite and sodium hydroxide to establish a pH of 10.5. However even with this high concentration of ascorbic acid the rate of formation of developed silver was considerably slower compared to a conventional hydroquinone lith developer. As a result the slope of the characteristic or sensitometric curve was appreciably lower than with hydroquinone. Eventually no commercially usable developer resulted from Zwicky's formula.

In European Patent Application No 91200311.8 it was shown that an excellent lith effect and at the same time a sufficient development activity could be obtained with developers combining a high pH (> 12.0) and a high concentration (> 0.4 mole/l) of a sugar derivative, corresponding to following general formula (I) :



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wherein X represents an oxygen atom or an imino group, and n represents a positive integer from 1 to 4, and

10 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.

According to said application preferred compounds corresponding to formula (I) were l-ascorbic acid and iso-ascorbic acid.

15 However according to experimental evidence developing solutions containing this kind of developing agents pose severe problems concerning the stability of their development activity. The active developing species are likely to be the mono- and dianion of ascorbic acid as was described by Willis and Pontius in Phot. Sci. Eng. Vol. 14 (6), p. 384 (1970), and their concentration is pH dependent. When oxidation occurs due to aerial oxygen or to the development reaction itself, the ascorbic acid molecule is broken down to oxidation products, a.o. oxalic acid, showing a higher acidity. In this way the concentration of the active developing agent and the pH are both lowered. It can be expected that ascorbic acid analogues will show similar oxidation reactions. However according to the European Patent Application cited above the successful production of a lith effect and of a satisfactory sensitometry is dependent both on a high pH and a high concentration of the developing agent. As a consequence developing solutions of this kind lose their good properties too quickly in the case of intensive continuous development and/or long exposure to air.

20 It is an object of the present invention to provide developing solutions for the development of photographic materials containing silver halide emulsion(s), with an improved stability in time of their development activity.

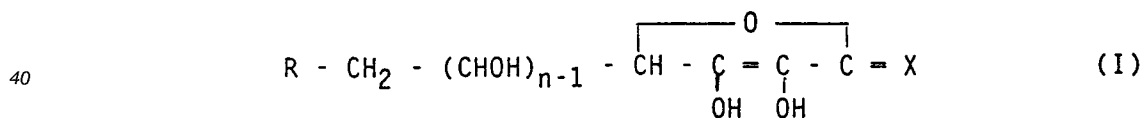
25 It is a further object of the present invention to provide developers containing a developing agent of the ascorbic acid type with a diminished drop in pH and active developing species concentration in function of time.

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3. Summary of the invention.

The objects of the present invention are realized by providing a silver halide developing solution characterized by a pH of at least 12.0 and containing :

35 - (a) a sugar derivative or an alkali metal salt thereof, present in a concentration of more than 0.4 mole/liter and corresponding to following general formula (I) :



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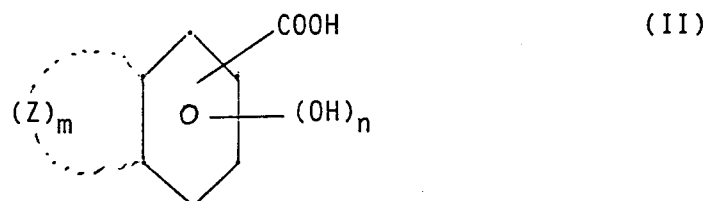
wherein X represents an oxygen atom or an imino group, and n represents a positive integer from 1 to 4, and

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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.

- (b) a compound corresponding to general formula (II), or an alkali metal salt thereof :

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wherein Z represents the necessary atoms to form a benzocondensed ring, $m = 0$ or 1 , and $n = 1, 2$ or 3 .

Surprisingly by the use of this combination a strong improvement in the stability of this type of developer was obtained.

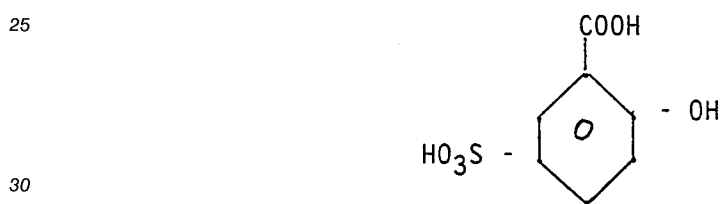
5 Preferred sugar derivatives corresponding to general formula (I) are l-ascorbic acid and iso-ascorbic acid.

4. Detailed description of the invention.

10 Preferred hydroxy-substituted aromatic carboxylic acids corresponding to general formula (II) for use in accordance with the present invention include :



II-1 (salicylic acid)



II-2 (sulphosalicylic acid)

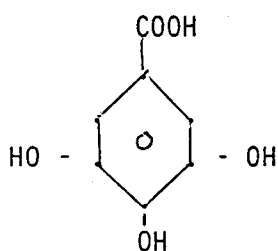
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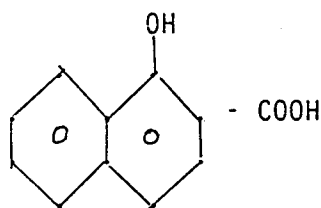
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II-3 (gallic acid)



II-4 (1-hydroxy-2-naphthoic acid)

25 The most preferred hydroxy-substituted aromatic carboxylic acid for use in accordance with the present invention is salicylic acid.

The hydroxy-substituted aromatic carboxylic acid is preferably present in the developing solution in a concentration ranging from 0.05 mole/liter to 0.7 mole/liter.

30 The sugar derivatives serving as developing agents in the practice of this invention are preferably present in a concentration ranging from 0.45 to 0.90 moles per liter. As stated above preferred compounds for application in the present invention are L-ascorbic acid and iso-ascorbic acid. Other useful analogous compounds include imino-L-ascorbic acid, 6-desoxy-L-ascorbic acid, L-rhamnoascorbic acid, L-fucoascorbic acid, d-glucoheptoascorbic acid, d-glucoascorbic acid and L-erythroascorbic acid. These compounds can be dissolved into the developing solution in their free acid form ; alternatively they can be incorporated as alkali salt, preferably the sodium or potassium salt or a mixture of both. In case of the latter method a lower amount of alkali hydroxide is needed to establish a pH of at least 12.0.

35 To achieve the optimal sensitometric and dot quality results of the present invention there is no need for a second auxiliary developing agent. Sulphite ions too can be omitted thanks to the stabilizing effect of the hydroxy-substituted aromatic carboxylic acid. So in a most preferred embodiment of the invention there are substantially no second developing agent and no sulphite ions present in the developer liquid, making it more ecologically safe.

In a preferred embodiment of the present invention an alkali bromide salt, e.g. potassium bromide is present in the developing solution preferably in a concentration ranging from 0.05 moles to 0.8 moles per liter and most preferably in a range from 0.1 to 0.4 moles per liter.

45 In an other preferred embodiment of the present invention at least one so-called antifogging agent or stabilizer is present in the developing solution. Numerous chemical classes of stabilizers are known in the photographic art as disclosed in Research Disclosure, Item 307105, nov. 1989, Chapter VI. Preferably the antifogging agent is a mercapto-group containing heterocyclic substance and most preferably it is 1-phenyl-5-mercapto-tetrazole in a concentration range from 10 mg/l to 1 g/l and most preferably in a range from 20 to 250 mg/l.

50 The rather high pH values in connection with the present invention can be established by means of conventional buffering agents but preferably for ecological reasons the pH is simply established by the presence of an alkali hydroxide, e.g. sodium or potassium hydroxide. The full benefits of this invention are obtained in a pH range from 12.3 to 13.5.

55 Other adjuvants well known to those skilled in the art may be added to the developer liquid of the present invention. 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. ethylene diamine

tetraacetic acid and analogues 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 alkonolamines and hardening agents including latent hardeners.

The developing solutions of the present invention can be employed to develop various types of photographic black-and-white materials, e.g. amateur and professional materials for still photography, radiographic recording and duplicating materials, cinematographic recording and duplicating materials, and microfilm. However the merits of the present invention become most obvious in developing camera or duplicating materials for graphic arts in view of the importance of exact reproduction of line edge and screen dot originals.

The emulsions present in these photographic materials can be of any halide composition, e.g. bromide, chloride, chlorobromide, iodobromide and chloriodobromide emulsions. The emulsions can belong to the negative working type or to the direct positive type, e.g. the externally fogged type or the unfogged type requiring a fogging agent in the material or in the developing solution. The best results are obtained however when applying the developing solutions of the invention on materials containing negative chlorobromide emulsions as is commonly the case in various types of graphic arts materials.

The photographic elements which can be developed by the liquids of the present invention can be composed of one single emulsion layer, as it is the case for many applications, or they can be built up by two or even more emulsion layers. Beside the light sensitive emulsion layer(s) the photographic material can contain several non-light sensitive layers, e.g. a protective layer, one or more backing layers, one or more subbing layers, and one or more intermediate layers, e.g. filter layers.

The emulsions present in the photographic materials which can be developed by the solutions of the present invention can be chemically sensitized as described e.g. in "Chimie et Physique Photographique" by P. Glafkides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature chemical sensitization can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines. The emulsions can be sensitized also by means of gold-sulphur ripeners or by means of reductors e.g. tin compounds as described in GB 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds.

The silver halide emulsions can be spectrally sensitized with methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes and complex merocyanine dyes. Infra-red sensitizing dyes and combinations with supersensitizing compounds can be present.

The silver halide emulsions can be stabilized by representatives of the same chemical classes which can be present in the developing solutions. Preferred compounds include triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58.

The gelatin binder of these photographic elements can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1,3-vinylsulphonyl-2-propanol, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methylol-dimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binder can also be hardened with fast-reacting hardeners such as carbamoyl-pyridinium salts as disclosed in US 4,063,952 and with the onium compounds as disclosed in European Patent Application No 90.201850.6

The photographic elements under consideration may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Preferred surface-active coating agents are compounds containing perfluorinated alkyl groups.

The photographic elements may further comprise various other additives such as e.g. compounds improving the dimensional stability of the photographic element, UV-absorbers, spacing agents and plasticizers.

As stated above the photographic material can contain several non light sensitive layers, e.g. an anti-stress top layer, one or more backing layers, and one or more intermediate layers eventually containing filter-or antihalation dyes that absorb scattering light and thus promote the image sharpness. Suitable light-absorbing dyes are described in e.g. US 4,092,168, US 4,311,787, DE 2,453,217, and GB 7 907 440. One or more backing layers can be provided at the non-light sensitive side of the support. These layers which can serve as anti-curl layer can contain e.g. matting agents like silica particles, lubricants, antistatic agents, light absorbing dyes, opacifying agents, e.g. titanium oxide and the usual ingredients like hardeners and wetting agents.

The support of the photographic material may be opaque or transparent, e.g. a paper support or resin support. When a paper support is used preference is given to one coated at one or both sides with an Alpha-olefin polymer, e.g. a polyethylene layer which optionally contains an anti-halation dye or pigment. It is also possible to use an organic resin support e.g. cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film, polycarbonate film, polyvinylchloride film or poly-Alpha-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.07 and 0.35 mm. These organic resin supports are preferably coated with a subbing layer which can contain water insoluble particles such as silica or titanium dioxide.

The photographic material to be developed by the solutions of the present invention can be image-wise exposed by any convenient radiation source in accordance with its specific application.

For processing preferably an automatically operating apparatus is used provided with a system for automatic replenishment of the processing solutions.

The development step can be followed by a washing step, a fixing solution and another washing or stabilization step. Finally the photographic material is dried. The first washing step can be omitted if wanted.

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

EXAMPLE 1

A developing solution was prepared consisting of :

sodium iso-ascorbate.H ₂ O	100 g
potassium bromide	30 g
1-phenyl-5-mercaptotetrazole	70 mg
water to make	1 l
pH adjusted to 12.7 with KOH	

To this basic solution were added 0.36 moles of organic acids or reductones as indicated in table 1. In each case the pH was readjusted to 12.7. Additional comparison examples were prepared by the addition to the basic solution of 0.36 mole of potassium sulphite, and 0.36 mole of sodium iso-ascorbate.H₂O respectively. From each sample one liter was brought into cylindrical glass tubes with a diameter of 6 cm and a bottom consisting of a sintered glass disk. The tubes were thermostated at 30° C. Through these solutions were pumped 120 l of dry air. The pH was measured before and after this treatment. The pH difference is a measure for the resistance to oxidation of the developing solution; the smaller this difference the better the oxidation resistance. The results are presented in table 1.

TABLE 1

sample No	ingredient	pH difference
1	- (comparison)	1.15
2	potassium sulphite	0.99
3	sodium iso-ascorbate.H ₂ O	0.94
4	gluconic acid	1.12
5	glucose	1.15
6	citric acid	1.07
7	pyrogallol	3.02
8	pyruvic acid	1.83
9	salicylic acid	0.56
10	sulpho-salicylic acid	0.54

The results of table 1 clearly demonstrate the beneficial effect of the compounds used in accordance with the invention (samples 9 and 10) on the oxidation resistance while the organic acids and reductones not belonging to the invention show no positive effect.

EXAMPLE 2

Sample 9 of the previous example, containing 0.36 mole/l of salicylic acid, was prepared again. Two volumetric flasks were filled to the top with this solution. One flask was stoppered from the air, the other remained unclosed. Two other flasks were filled with a comparison solution containing no salicylic acid. On of them was also stoppered from the air, the other was not.

After 20 days the pH and the sodium iso-ascorbate.H₂O concentration were determined analytically. The results are summarized in table 2 :

TABLE 2

sample salicylic acid	stoppered	pH	sodium iso-ascorbate.H ₂ O (g/l)
-	-	11.3	67
-	+	12.2	71
+	-	12.6	100
+	+	12.7	100

The results of table 2 show that in the absence of salicylic acid a decline of sodium iso-ascorbate.H₂O concentration occurs even when the flask is stoppered; on the contrary in the presence of salicylic acid no loss occurs in both cases.

EXAMPLE 3

A silver halide emulsion containing 83.6 % of chloride, 16 % of bromide and 0.4 % of iodide was prepared by a double jet technique. The emulsion contained 0.1 ppm of Rhodium per mole of silver halide. The average grain size was 0.27 micron. The emulsion was chemically sensitized with ammonium gold(III) thiocyanate and sodium thiosulphate, stabilized with 4-hydroxy-6-methyl-(1,3,3a,7)-tetraazaindene and spectrally sensitized to the blue and green spectral region.

The emulsion was coated onto a subbed polyethylene terephthalate support at a gelatin coverage of 3.1 g per m², and a coverage of silver halide equivalent to 4.0 g of silver per m². A protective layer was applied containing formaldehyde-hardened gelatin at a coverage of 1 g per m².

Samples of the thus prepared material were contact exposed in a KLIMSCH VACUPRINT 65 S through a continuous tone wedge. The exposed samples were processed for 30 s at 30 °C in developers 1 and 9 of example 1, containing no salicylic acid and 0.36 mole of salicylic acid respectively. After development the samples were fixed, washed and dried.

The sensitometric results are represented in table 3.

In said table the photographic speed is expressed in relative arithmetic values (rel. S) measured at density 3.0 above fog wherein the value of the comparison is arbitrarily set to 100: higher number means higher sensitivity. Gradient values in the toe (g_t) were measured between densities 0.1 and 0.6 above fog. Straight line gradients (grad) were determined between densities 0.3 and 3.0 above fog. Gradient values in the shoulder (g_s) were measured between densities 3.0 and 3.8 above fog.

TABLE 3

devel. sol .	sensitometry				
	fog	rel.S	g_t	grad	g_s
comparison	0.07	100	5.3	13.8	6.8
+ salicylic acid	0.07	90	5.7	10.9	17.1

It is clear from table 3 that the sample developed in the solution according to the invention shows the better over-all gradation especially in the shoulder.

EXAMPLE 4

Ten samples of the photographic material described in example 3 were exposed and processed in the two same developers of example 3, for 30 s at 30 °C in a RAPILINE 66, a continuous rapid access processing apparatus marketed by AGFA-GEVAERT N.V..

The difference between the highest and lowest sensitivity value is taken as a measure for the short term stability of the developers. The sensitivity is measured at density 3.0 above fog and is expressed as a relative logarithmic value.

For the comparison developer this maximal sensitivity difference was 0.07 log Et. On the contrary for the developer containing salicylic acid this maximal speed difference was only 0.03 log Et.

EXAMPLE 5

A RAPILINE 66 processing machine was filled with the respective developers of example 3. During a period of 30 days 4 sq.m of the photographic material described in example 3 were fully exposed and processed each day. For replenishment 2000 ml developer per day and an additional 250 ml per sq.m. were added.

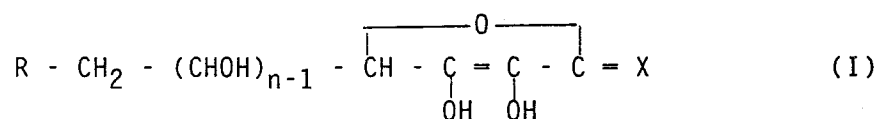
After this daily troughput program samples of the photographic material were sensitometrically exposed and processed. The sensitivity was measured as in previous example.

The difference between the highest and lowest sensitivity values obtained over a period of 30 days was taken as a measure for the long term stability of the developing solution.

For the comparison developer this speed difference was 0.24 log Et. For the developer containing salicylic acid this speed difference was limited to 0.11 log Et.

Claims

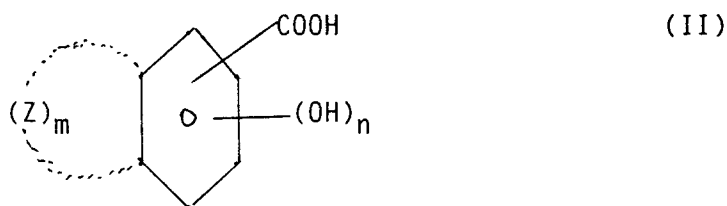
- Silver halide developing solution characterized by a pH of at least 12.0 and containing :
 - (a) a sugar derivative or an alkali metal salt thereof, present in a concentration of more than 0.4 mole/liter and corresponding to following general formula (I) :



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.

- (b) a compound corresponding to general formula (II), or an alkali metal salt thereof :



wherein Z represents the necessary atoms to form a benzocondensed ring, $m = 0$ or 1 , and $n = 1, 2$ or 3 .

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2. Silver halide developing solution according to claim 1 wherein said sugar derivative is l-ascorbic acid or iso-ascorbic acid.

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3. Silver halide developing solution according to claim 1 or 2 wherein said compound according to general formula (II) is present in a concentration from 0.05 mole/l to 0.7 mole/l.

4. Silver halide developing solution according to any of claims 1 to 3 wherein said compound according to general formula (II) is salicylic acid.

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5. Silver halide developing solution according to any of claims 1 to 4 which contains no substantial amount of another developing agent.

6. Silver halide developing solution according to any of claims 1 to 5 which contains no substantial amount of sulphite ions.

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7. Silver halide developing solution according to any of claims 1 to 6 which further contains an alkali bromide in a concentration ranging from 0.1 to 0.4 moles per liter.

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8. Silver halide developing solution according to any of claims 1 to 7 which further contains a heterocyclic stabilizer.

9. Photographic developing solution according to claim 8 wherein said heterocyclic stabilizer in a mercapto-group containing heterocyclic stabilizer.

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10. Photographic developing solution according to claim 9 wherein said heterocyclic stabilizer containing a mercapto-group is 1-phenyl-5-mercaptotetrazole and said stabilizer is present in a concentration ranging from 20 to 250 mg/l.

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11. Method for developing an exposed photographic material containing a support and at least one silver halide emulsion layer in a solution according to any of claims 1 to 11.

12. Method according to claim 11 wherein said photographic material is a graphic arts material containing a chlorobromide emulsion.

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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-3 964 912 (H.J.PRICE) * column 11, line 60 - column 12, line 38 * ---	1-12	G03C5/305 G03C5/30
A	US-A-3 826 654 (G.R.WEISS) * column 3, line 68 - column 4, line 19 * * column 7, line 14 - line 17 * ---	1-12	
A	US-A-3 386 824 (A.MILLER) * column 4, line 18 - line 26 * ---	1-12	
A	US-A-4 569 904 (E.OKUTSU) * column 2, line 10 - line 12 * * column 3, line 6 - line 17 * * column 6, line 57 - column 8, line 15 * ---	1-12	
A	US-A-3 790 383 (I.SHIMAMURA ETV AL) * column 2, line 7 - line 19 * * abstract * ---	1-12	
A	GB-A-1 182 198 (EASTMAN KODAK COMPANY) * page 1, right column, line 64 - line 75 * ---	1-12	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN vol. 5, no. 21 (P-48)(693) 7 February 1981 & JP-A-55 149 936 (FUJI SHASHIN FILM KK) 21 November 1980 * abstract * -----	1-12	G03C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07 MAY 1992	Examiner BOLGER W.
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