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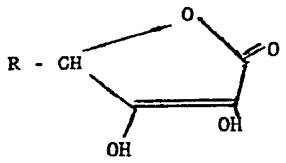
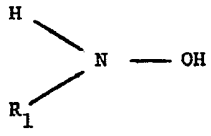
(54) Photographic developers

(57) A developing solution for processing black and white photographic comprises as a main developing agent (i) an ascorbic acid type compound of the general formula I:-



----- I

wherein R is a hydroxylated alkyl group having 1 to 4 carbon atoms or alkali metal salts of such compounds (ii) an electron transfer agent as a superadditive developing agent eg. a pyrazolidone or metal and (iii) a hydroxylamine of the general formula II:-



----- II

or salt thereof, wherein R_1 is hydrogen, an all group having 1 to 4 carbon atoms which may be substituted, an aryl group which may be substituted, together with an alkali to bring the pH of the developing solution above 8.

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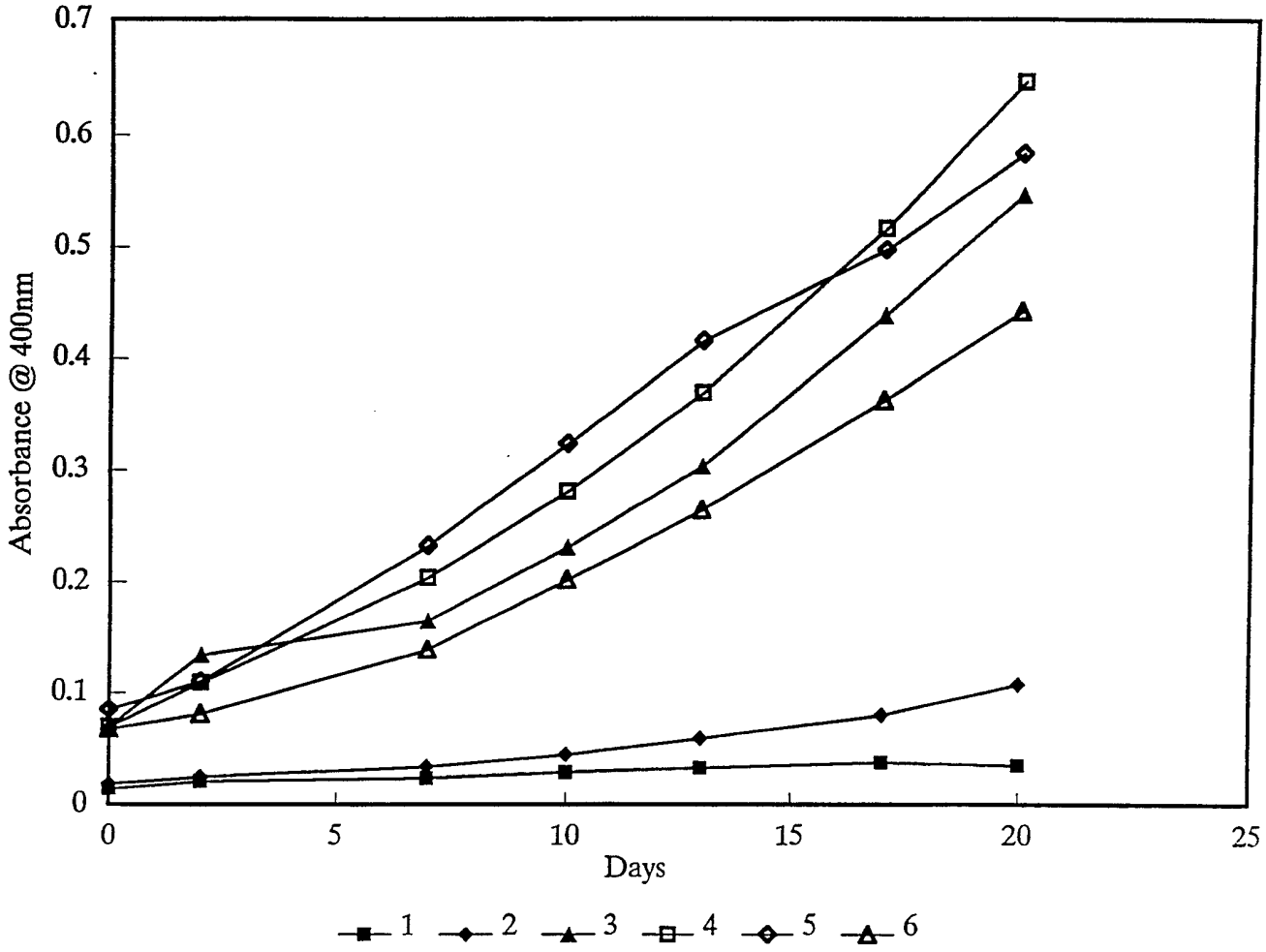
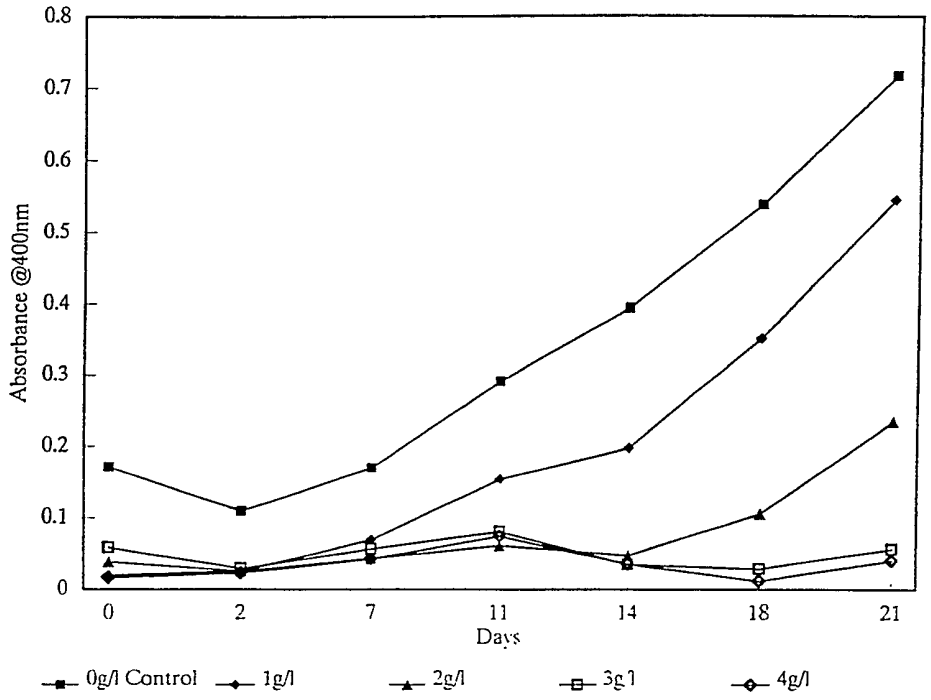
Figure 1



1=Hydroxylamine Hydrochloride
2=N-Methyl hydroxylamine hydrochloride
3=Standard developer
4=N,N-Diethylhydroxylamine
5=O-Methylhydroxylamine
6=Hydroxyurea

Figure 2

a) hydroxylamine hydrochloride



b) N-methyl hydroxylamine hydrochloride

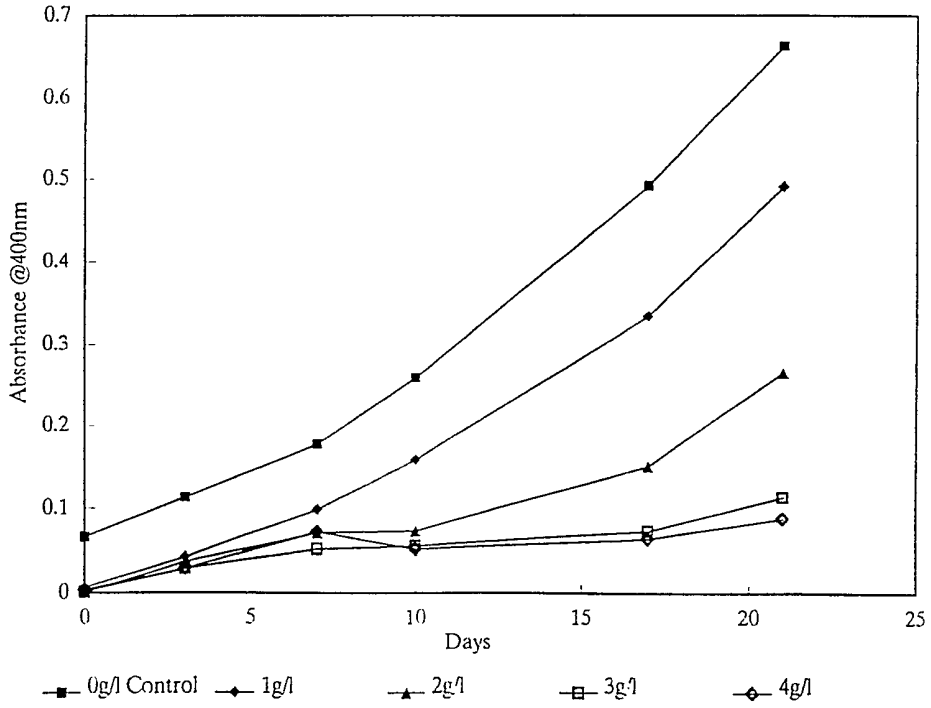
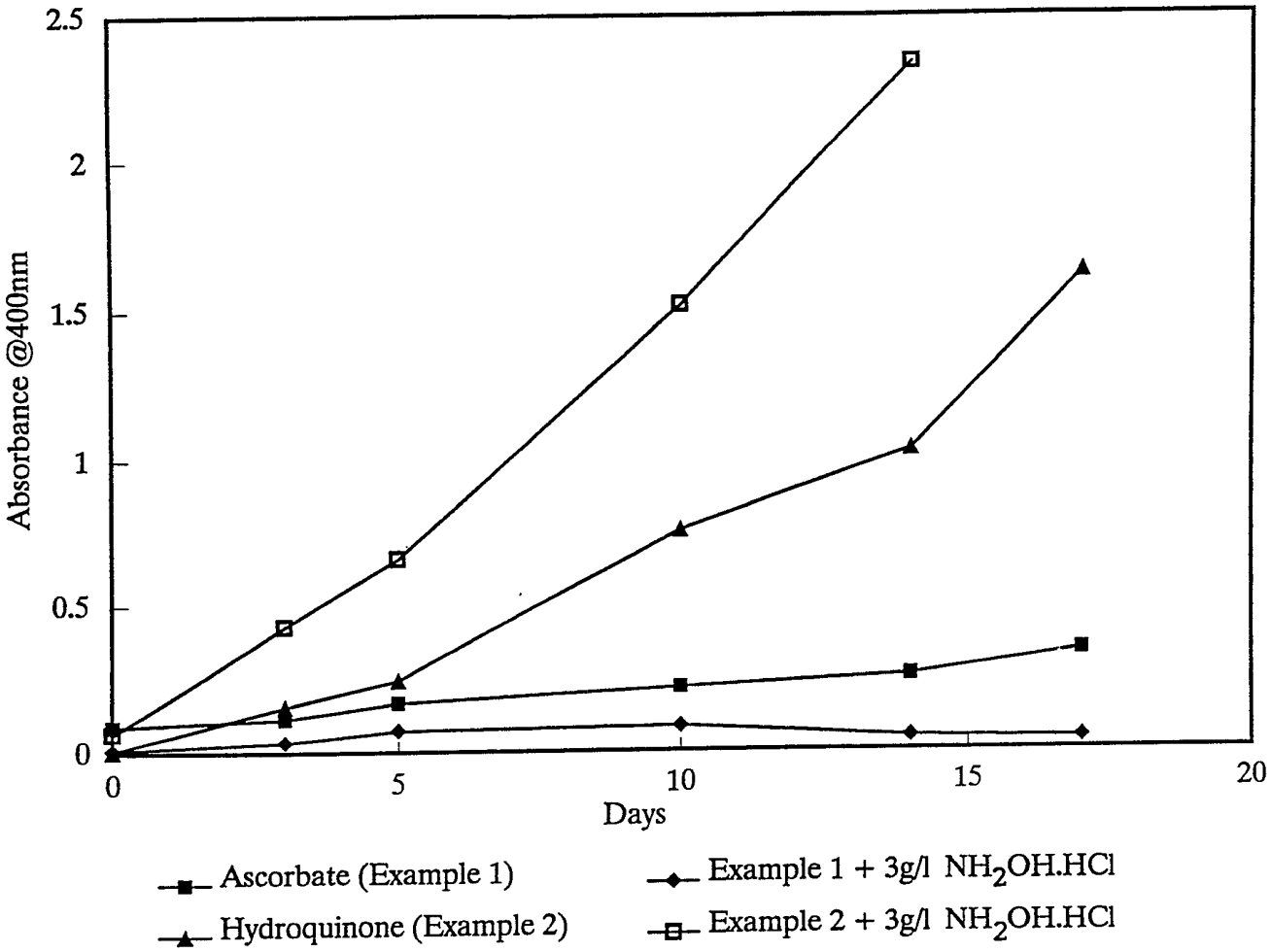


Figure 3


2.5
2
1.5
1
0.5
0
Absorbance @400nm
0
5
10
15
20
Days
Ascorbate (Example 1)
Hydroquinone (Example 2)
Example 1 + 3g/l NH2OH.HCl
Example 2 + 3g/l NH2OH.HCl

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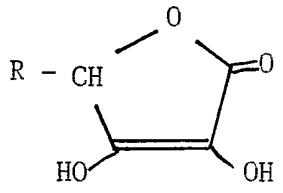
Entitled: Photographic Developing Solution

This invention relates to ascorbic acid based developing solutions for use with silver halide photographic materials.

Ascorbic acid based black and white developing solutions are being used to an increasing extent because ascorbic acid does not suffer from the same defects that hydroquinone could suffer from. However ascorbic acid based developing solutions are not free from defects and one of these defects is that solutions, especially ready-to-use solutions, ie not concentrated solutions, discolour very rapidly when exposed to atmospheric conditions at the basic pH necessary for photographic processing.

It is the object of the present invention to provide an additive which stabilises such solutions against the development of such discolouration.

Therefore according to the present invention there is provided a method of processing black and white photographic material in a working strength developing solution which comprises as the main developing agent an ascorbic acid type compound of the general formula I:-



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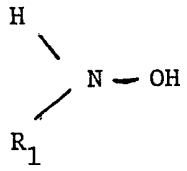
wherein R is a hydroxylated alkyl group having 1 to 4 carbon atoms or alkali metal salts of such compounds, and an electron transfer agent as a superadditive developing agent, in the presence of a hydroxylamine compound of the general formula II:-



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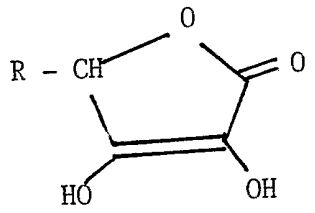
or a salt thereof, wherein R_1 is hydrogen, an alkyl group having 1 to 6 carbon atoms which may be substituted, an aryl group which may be substituted, together with an alkali to bring the pH of the developing solution above 8. Preferably the pH of the solution is in the range of 9.5 to 11.

Examples of substituents in the R_1 group are a water-solubilising group such as hydroxy, sulphonic acid or carboxylic acid groups. Examples of other substituents in the R_1 group are alkyl or aryl groups.

In one method of the invention the hydroxylamine compound of formula II is present in the ascorbic acid based working strength developing solution. In another method of the invention the hydroxylamine compound of formula II is present in the black and white photographic material which is being processed. A combination of these two methods may also be used.

According to a preferred embodiment of the invention there is provided a working strength black and white developing solution which comprises per litre of solution 5 to 15g of an ascorbic acid type compound of the general formula I:-



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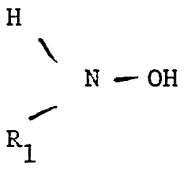
wherein R is a hydroxylated alkyl group having 1 to 4 carbon atoms or alkali metal salts of such compounds and an electron transfer agent as a superadditive developing agent, together with 1 to 5g of a hydroxylamine compound of the general formula II:-



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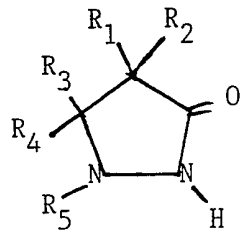
or a salt thereof, wherein R_1 is as defined above together with an alkali to bring the pH of the developing solution above 9.5.

Most preferably the pH of the developing solution is within the range of 9.5 to 11.

Preferred examples of ascorbic acid type compounds included in general formula I are L-ascorbic acid, and D-iso ascorbic acid. The preferred compounds of formula II are hydroxylamine and N-methyl hydroxylamine.

Most conveniently these hydroxylamines are added to the solution as their hydrochloric acid salt as the hydrochloric acid salts of these hydroxylamines are the commercially available compounds. Alternatively the salts with sulphuric acid or other convenient acids may be used. It is to be understood that under the pH conditions of use such salts substantially revert to the free hydroxylamine compound. It is also to be understood that under the pH conditions of use the ascorbic acid compound is substantially in the anionic form.

The preferred electron transfer agents which act as super-additive developing agents are metol and pyrazolidinone compounds of the general formula III



- - - - - III

wherein R_1 and R_2 are each hydrogen, alkyl groups having 1 to 4 carbon atoms or hydroxy alkyl groups having 1 to 4 carbon atoms, R_5 is an aromatic ring which is optionally substituted and R_3 and R_4 are each hydrogen, alkyl groups having 1 to 4 carbon atoms or phenyl.

Preferably there is present in the working strength black and white developing solution as just set forth an alkali metal sulphite. Most preferably potassium sulphite or sodium sulphite are used. A suitable concentration of alkali metal sulphite is from 5 to 20 g/litre.

Preferably the pH of the ready to use developing solution is about 10.1 to 10.4 and sufficient sodium or potassium carbonate is present in developing solution to attain this pH range. Alternatively a suitable pH may be achieved by the use of caustic alkali, or borate or other basic salts.

Other classes of compound which may be present in the developing solution include restrainers such as potassium bromide, antifoggants such as benzotriazole compounds, and sequestering agents such as ethylenediamine tetra-acetic acid, (EDTA) diaminopropanol tetraacetic acid (DAPTA) and diethylenetriamine pentaacetic acid (DTPA), or phosphonic acids such as 1-hydroxyethylidene 1,1-diphosphonic acid, diethylenetriamine penta (methylene phosphonic acid), ethylenediamine tetra (methylene phosphonic acid) and nitrolotris (methylene phosphonic acid) and alkali metal salts thereof.

When the compound of formula II is present in the black and white developing solution as just set forth the discolouration of the solution to an unacceptable level is delayed for at least 20 days at ambient temperature. This is shown in the Example which follows.

The Example I which follows also shows that a large number of hydroxylamines and related compounds not covered by formula II were tested in the developing solution instead of the compounds covered by formula II but none of these increased the period of acceptable colour change to the same extent as the compounds of formula II. Examples of these compounds not covered by formula II are hydroxyurea, O-methylhydroxylamine, N,N diethylhydroxylamine, benzoylhydroxamic acid, salicylhydroxamic acid, and hydroxylamine-O-sulphonic acid.

A number of hydroxylamines have been used as preservatives in colour developing solutions which of course have an entirely different formulation to the black and white developing solutions as just set forth. In particular N,N-diethylhydroxylamine has found great commercial use as a preservative in colour developing solutions but as stated above this compound does not act when present in the ascorbic acid developing solutions as just set forth to delay the onset of an unacceptable colouration. It is a surprising and novel feature of the present invention that the effect is restricted to the compounds of formula II, and that similar compounds do not show the effect, even those such as N,N-diethyl hydroxylamine which has been used in colour developing solutions.

To some extent hydroquinone based developing solution discolour over a period of days but not to the same extent as ascorbic acid based developing solutions. However, when the compounds of formula II were added to hydroquinone based developing solutions a large increase in the rate of discolouration of the developing solutions was observed, and this invention is therefore not of use in hydroquinone based developing solutions.

The preferred superadditive developer of formula III is 1-phenyl-4-methyl-4-hydroxymethyl-pyrazolidin-3-one which is hereinafter referred to as developing agent A. Most preferably this is present in the working strength developing solution at a concentration of 0.2 to 0.8g/litre

The preferred compounds of formula II, which as hereinbefore stated are hydroxylamine hydrochloride and N-methyl hydroxylamine hydrochloride, can be added to the ready-to-use developing solution as solids.

Alternative compounds of formula II in which the group R is substituted by carboxylic or sulphonic acid groups may be prepared by the methods mentioned in Belgian Patent 558 501.

The accompanying Examples will serve to illustrate the invention.

Example I

The following ascorbate based developing solution was prepared:-

Potassium sulphite (65% w/v)	$15cm^3$
DTPA Na_5 (37% w/v)	$6.8cm^3$
Developing Agent A	0.5g
Sodium-L-Ascorbate	10g
Potassium Bromide	1g
Benzotriazole	0.02g
Potassium Carbonate	20g
Water ->	1L

pH 10.50

To litre portions of this solution these were added

Hydroxylamine hydrochloride	7g
N-methyl hydroxylamine hydrochloride	7g
Standard - no addition	-
N, N diethylhydroxylamine	5g
O-methyl hydroxylamine	5g
Hydroxyurea	5g

These solutions were left standing for 20 days and the colour of the solutions was measured initially and then every five days. The change in light absorbance at 400nm was determined.

An absorbance of 0.1 is a light yellow colour but an absorbance of 0.6 is a dark yellow to orange colour.

These results are shown in figure 1.

From these results it can be seen that only hydroxylamine hydrochloride and N-methyl hydroxylamine hydrochloride are effective in preventing an unacceptable increase in colour of the developing solution.

Figure 2 shows the effect of different concentrations of hydroxylamine hydrochloride and N-methyl hydroxylamine hydrochloride on the developer solution of Example 1. From these it can be seen that even the lowest levels of addition of these compounds give a remarkable reduction in the colouration of freshly prepared solutions, and that a level of around 3g/litre of either compound prevents noticeable discolouration from occurring over a period of at least 15 days.

EXAMPLE 2

The ascorbate based developing solution as set out in example I was prepared. To 1 litre nothing was added, to a second 1 litre portion $3gl^{-1}$ hydroxylamine hydrochloride was added.

A hydroquinone based developing solution was prepared:

DTPA Na_5 (37% w/v)	$6.8cm^3$
Sodium sulphite	12g
Potassium carbonate	15g
Hydroquinone	3.5g
Developing Agent A	0.25g
Potassium bromide	0.7g
Benzotriazole	0.03g
Sodium hydroxide (67% w/v)	$1.2cm^3$
water ->	1 L

pH -> 10.80

To 1 litre nothing was added, to a second litre portion $3gl^{-1}$ hydroxylamine hydrochloride was added.

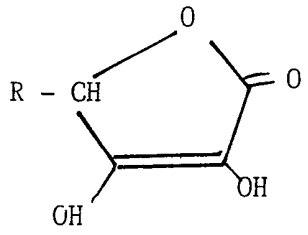
These four solutions were left standing for 17 days and the colour of the solution was measured at periodic intervals. The change in light absorbance at 400nm was determined and the results obtained are shown in figure 3.

It can be seen that while the addition of hydroxylamine hydrochloride is very effective in preventing an unacceptable increase in colour of the developer solution based on ascorbate, this addition is in fact detrimental to the solution colour of the hydroquinone based developer.

This result illustrates that this invention is of no use in hydroquinone based developing solutions.

Claims

1. A method of processing black and white photographic material in a developing solution which comprises as a main developing agent an ascorbic acid type compound of the general formula I:-



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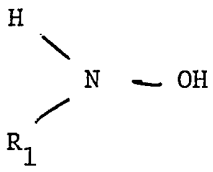
wherein R is a hydroxylated alkyl group having 1 to 4 carbon atoms or alkali metal salts of such compounds and an electron transfer agent as a superadditive developing agent, in the presence of a hydroxylamine compound of the general formula II:-



- - - - - II

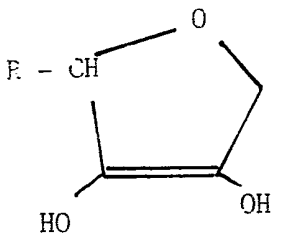
or a salt thereof, wherein R_1 is hydrogen, an alkyl group having 1 to 4 carbon atoms which may be substituted, an aryl group which may be substituted, together with an alkali to bring the pH of the developing solution above 8.

2. A method according to claim 1 wherein the compound of formula II is hydroxylamine hydrochloride or N-methyl hydroxylamine hydrochloride.

3. A method according to either claim 1 or claim 2 wherein the compound of formula II is present initially in the working strength ascorbic acid based developing solution.

4. A method according to either claim 1 or claim 2 wherein the compound of formula II is present in the black and white photographic material being developed.

5. A black and white working strength photographic developing solution which comprises per litre of solution 5 to 15g of an ascorbic acid type compound of the general formula I:-



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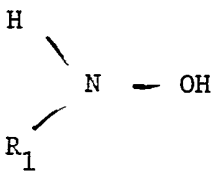
wherein R is a hydroxylated alkyl group having 1 to 4 carbon atoms or alkali metal salts of such compounds, an electron transfer agent as a superadditive developing agent, and a hydroxylamine compound of the general formula II:-



- - - - II

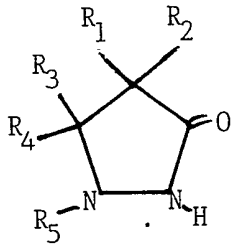
or a salt thereof, wherein R_1 is hydrogen, an alkyl group having 1 to 4 carbon atoms which may be substituted, an aryl group which may be substituted, together with an alkali to bring the pH of the developing solution above 8.

6. A black and white developing solution according to claim 5 wherein the pH is within the range of 9.5 to 11.

7. A black and white developing solution according to claim 5 wherein the ascorbic acid of formula I is L-ascorbic acid or D-iso ascorbic acid.

8. A black and white developing solution according to claim 5 wherein the hydroxylamine compound of formula II is hydroxylamine hydrochloride or N-methyl hydroxylamine hydrochloride.

9. A black and white developing solution according to claim 5 wherein the electron transfer agent which acts as a super-additive developing agent is metol or a pyrazolidinone compound of the general formula III:-



- - - - - III

wherein R_1 and R_2 are each hydrogen, alkyl groups having 1 to 4 carbon atoms or hydroxy alkyl groups having 1 to 4 carbon atoms, R_5 is an aromatic ring which is optionally substituted and R_3 and R_4 are each hydrogen, alkyl groups having 1 to 4 carbon atoms or phenyl.

9. A black and white developing solution according to claim 9 wherein the pyrazolidinone compound of formula III is 1-phenyl-4-methyl-4-hydroxy-methyl-pyrazolidin-3-one.

10. A black and white developing solution according to claim 5 which comprises from 5 to 20g/litre of an alkali metal sulphite.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
GB 9323925.9

Relevant Technical Fields

(i) UK Cl (Ed.M) G2C - CC20BM

(ii) Int Cl (Ed.5) G03C

Search Examiner
M K B REYNOLDS

Date of completion of Search
8 DECEMBER 1994

Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) DERWENT WPI

Documents considered relevant following a search in respect of Claims :-
1 TO 10

Categories of documents

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P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
A	GB 2027920 A	(KODAK) Example 2	
A	GB 958678	(KODAK) page 2 lines 14 to 20, page 2 line 83 to pages 3 to 103	

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